VOL. X. [MAY, 1888.] No. 3.

AMERICAN CHEMICAL JOURNAL.

Contributions from the Chemical Laboratory of Harvard College.

LV.—THE ACTION OF FLUORIDE OF SILICON ON ORGANIC BASES.[1]

BY ARTHUR M. COMEY AND C. LORING JACKSON.

The research described in the following paper was undertaken in the hope of obtaining from the amines products similar to the compound which ammonia gives with fluoride of silicon, $(NH_3)_2SiF_4$, discovered by Gay-Lussac and Thenard,[2] and three years later prepared and studied by J. Davy.[3] We have been able to find only two previous papers on this subject, one published by Laurent and Delbos,[4] in 1848, in which the action of fluoride of silicon on aniline is described, the product being a nearly white mass, which they washed with ether, boiled with alcohol, and sublimed to purify it for analysis; their analyses, however, led only to a very complex formula containing oxygen, which they advance "with much reserve," although it was confirmed by the proportions[5] in which its factors combined. The substance when treated with water gave a gelatinous precipitate of silicic acid, and when boiled with alcohol was converted into small white

[1] Communicated by the authors, from the Proceedings of the American Academy of Arts and Sciences.

[2] Mém. d'Arcueil 2, 317.

[3] Phil. Trans. 1812, p. 352.

[4] Ann. chim. phys., ser. 3, 22, 101.

[5] These proportions agree tolerably with the formula worked out by us for this substance, but their analytical results do not, and are entitled to no consideration, on account of the difficulties in the analysis, which Laurent and Delbos did not succeed in overcoming.

lustrous scales.[1] The second paper was published by W. Knop,[2] in 1858, and had for its primary object the study of the solution of fluoride of silicon in absolute alcohol, which gave with urea and aniline the fluosilicates of these bases, both of which Knop sublimed, and obtained from the urea fluosilicate only ammonic fluosilicate, silicic acid, and cyanuric acid; but from the aniline fluosilicate a new substance, which gave a precipitate of gelatinous silicic acid with water, and contained more silicon and fluorine than the fluosilicate. He did not, however, identify it with the substance made by Laurent and Delbos. We may add, that some years later W. Knop and W. Wolf[3] describe the aniline fluosilicate more in detail.

The results of our work on this subject may be summarised briefly as follows. Aniline forms with fluoride of silicon a compound having the formula $(C_6H_5NH_2)_3(SiF_4)_2$, which sublimes without alteration, but is decomposed with water, forming aniline fluosilicate and silicic acid; when heated with an excess of aniline it is converted into another compound having the formula $(C_6H_5NH_2)_4(SiF_4)_3$, and the same substance is formed when fluoride of silicon acts on aniline at high temperatures. This second product is unstable, breaking up spontaneously into the first and free aniline. The following bases also give compounds containing three molecules of the base to two of fluoride of silicon: paratoluidine, orthotoluidine, parachloraniline, diphenylamine, dimethylaniline, chinoline, and dimethylamine, the last giving also a compound having the formula $[(CH_3)_2NH]_4(SiF_4)_2$. On the other hand, we have not succeeded in obtaining from ammonia a compound of the formula $(NH_3)_3(SiF_4)_2$.

We propose to call these substances silicotetrafluorides, a clumsy name, it is true, but one which will designate them with certainty, whereas all the simpler names, such as silicofluoride or fluosilicide, have been used for the fluosilicates at one time or another, and might therefore lead to confusion.

The remainder of the paper contains the detailed account of our experimental results, and at the end a discussion of our views in regard to the constitution of the silicotetrafluorides.

Products of the Action of Fluoride of Silicon on Aniline.

Trianiline disilicotetrafluoride, $(C_6H_5NH_2)_3(SiF_4)_2$.—This substance was prepared by passing fluoride of silicon over aniline.

[1] Aniline fluosilicate. [2] Chem. Centralblatt, 1858, p. 388. [3] Ibid. 1862, p. 401.

The fluoride of silicon was made in the usual way, from calcic fluoride, sand, and sulphuric acid; but as we found that a glass flask after using it two or three times became perforated by the small quantities of hydrofluoric acid formed in the process, we replaced it by a thick glass bottle warmed in a water-bath, which lasted through a number of preparations. The delivery tube should not dip below the surface of the aniline, as in that case there is danger that it will be stopped by the product; but if it is brought near the surface of the base, the action takes place so rapidly that very little of the fluoride of silicon is lost. A good deal of heat is given out during the reaction, and the aniline is converted into a loose white solid, which was washed with hot ligroine until free from aniline, and then its purification finished by two sublimations. The yield was essentially quantitative, 30 grams of aniline giving after treatment with fluoride of silicon for 24 hours 51 grams of product, instead of 52 grams, the amount which should be obtained for the formula[1] $(C_6H_5NH_2)_3(SiF_4)_2$. The same substance is formed when aniline fluosilicate is sublimed, and the preparation, the analysis of which is numbered I, was made in this way. It is to be observed that the substance analysed by Laurent and Delbos was really prepared in this way, since by boiling their original product with alcohol they converted it into aniline fluosilicate, which was afterward reconverted into the silicotetrafluoride by sublimation. Also the substance obtained by Knop by sublimation of his aniline fluosilicate was the trianiline disilicotetrafluoride.

The method of analysis used for all these substances consisted in neutralising a weighed quantity of the substance dissolved in hot water in a platinum dish with a standard solution of sodic hydrate, using a solution of litmus as the indicator. The liquid was then heated to boiling, more of the sodic hydrate added, if the reaction had become acid, and evaporated to dryness on the water-bath, the residue treated with water, and the silicic dioxide filtered out. The filtrate, after neutralising once more with the sodic hydrate, which is usually necessary when the organic base is one with an alkaline reaction, (NH_3 or $(CH_3)_2NH$), is treated with a solution of zincic oxide in ammonic carbonate, evaporated once more to dryness on the water-bath, treated with water, and filtered; the pre-

[1] Laurent and Delbos found that 59.5 grams of aniline absorbed 40.5 grams of fluoride of silicon. Our formula requires 44.3 grams.

cipitate is dissolved in strong nitric acid, evaporated to dryness, the residue after treatment with strong nitric acid extracted with water, and the silicic dioxide thus obtained added to that from the residue of the first evaporation, ignited, and weighed. The fluorine was usually calculated from the amount of the standard solution of sodic hydrate necessary for the neutralisation of the hydrofluoric acid present, but it was also occasionally determined direct in the filtrate from the zincic carbonate and silicate by evaporating to dryness in a platinum crucible, and, after removing any slight excess of sodic carbonate by converting it into acetate and washing with 80 per cent. alcohol, igniting and weighing as sodic fluoride.

I. 0.2686 gram of the substance gave 19.6 cc. of nitrogen at a temperature of 23° and a pressure of 768 mm.

II. 0.2982 gram of substance gave 0.0751 gram of silicic dioxide and 0.2105 gram of sodic fluoride.

III. 0.2842 gram of substance gave 0.0717 gram of silicic dioxide and 0.1968 gram of sodic fluoride.

IV. 0.3784 gram of substance needed for neutralisation 0.2480 gram of sodic hydrate.

	Calculated for $(C_6H_5NH_2)_3(SiF_4)_2$.	Found. I.	II.	III.	IV.
Nitrogen	8.62	8.31			
Silicon	11.50	...	11.75	11.77	
Fluorine	31.24	...	31.94	31.33	31.15

Several attempts to make a combustion of the substance have shown that great difficulties stand in the way of getting satisfactory results, and, as the determinations of nitrogen, silicon, and fluorine just given are sufficient to establish its formula beyond a doubt, we have not thought it worth while to devote to the study of the conditions of its combustion the time necessary to obtain an accurate result.

Properties.—The trianiline disilicotetrafluoride is a white semi-crystalline to amorphous solid, which sublimes in the neighborhood of 200° without melting. It is insoluble in ether (anhydrous), benzol, ligroine, chloroform, or carbonic disulphide. It is decomposed very slowly by boiling absolute alcohol without any deposition of silicic acid, and converted into aniline fluosilicate; we have not succeeded in bringing the other product of this reaction into a state fit for analysis; it is a thick liquid, probably a silicic ethyl-ester. The action is more rapid with alcohol containing water.

Water decomposes it at once with deposition of silicic acid, and the solution yields on evaporation aniline fluosilicate[1] in beautiful white pearly scales. Its identity was determined by the following analysis:

0.7488 gram of substance gave by precipitation with baric chloride 0.6372 gram of baric fluosilicate.

	Calculated for $(C_6H_5NH_3)_2SiF_6$.	Found.
SiF_6	43.04	43.30

To determine the proportions in which the substances act on each other when water is added to the trianiline disilicotetrafluoride, we have studied the reaction quantitatively with the following results:

1.3092 grams of the substance were dissolved in water, and the silicic acid precipitated filtered out, ignited, and weighed, giving 0.1200 gram of silicic dioxide. To the filtrate was added potassic chloride, and the potassic fluosilicate formed was dried at 100° and weighed, giving 0.7370 gram.

These numbers agree best with the following reaction:

$$4(C_6H_5NH_2)_3(SiF_4)_2 + 6H_2O = 5(C_6H_5NH_3)_2SiF_6 + 2C_6H_5NH_3F + 3SiO_2,^2$$

as is shown by comparing the amounts of the products which would be obtained from 100 grams of trianiline disilicotetrafluoride according to it, and those which were actually obtained in the experiment just described.

	Calculated from the Reaction.	Found.
Silicic dioxide	9.25	9.17
Aniline fluosilicate	84.70	84.41

Two attempts were made also to determine the amount of aniline fluoride formed (both by titration and by conversion into calcic fluoride); but although these experiments proved the presence of a fluoride, they gave results which did not agree with each other or with the theory, the reason being without doubt that a portion of the aniline fluoride was converted into fluosilicate during the filtrations, which we had to carry on in a glass funnel.

The action of ammonia gas upon the trianiline disilicotetrafluoride was studied carefully, since we hoped that it might throw light

[1] W. Knop and W. Wolf, Chem. Centralblatt, 1862, p. 401.

[2] As a matter of fact, it was one of the silicic acids which was precipitated; but as we do not know which one it was, we prefer to write it as silicic dioxide.

on the constitution of this substance, and also that the corresponding ammonia compound $(NH_3)_8(SiF_4)_2$ might be formed. Neither of these hopes has been realised, however, for upon passing ammonia gas over the trianiline disilicotetrafluoride the compound was decomposed with a strong evolution of heat, aniline was set free, and the product was the compound of ammonia and fluoride of silicon already described by J. Davy, as was proved by the following analyses, which also show that none of the desired substance $(NH_3)_8(SiF_4)_2$ was formed; and as it was not obtained under these conditions, it is fair to suppose that it cannot exist. The substances for Analyses I and II were prepared by washing the aniline out of the crude product of the reaction with ligroine. The substance for Analysis III was further purified by sublimation.

I. 0.3414 gram of the substance gave 0.1496 gram of silicic dioxide and 0.4154 gram of sodic fluoride.

II. 0.4400 gram gave 0.1937 gram of silicic dioxide.

III. 0.3770 gram gave 0.1625 gram of silicic dioxide.

IV. 0.1920 gram gave 0.0840 gram of silicic dioxide.

	Calculated for $(NH_3)_4(SiF_4)_2$.	Found. I.	II.	III.	IV.
Silicon	20.29	20.44	20.55	20.12	20.41
Fluorine	55.07	55.03			

It was noticed during the purification of this substance that it sublimed at a much higher temperature than the trianiline disilicotetrafluoride. The reaction which takes place when trianiline disilicotetrafluoride is treated with ammonia gas is the following:

$$(C_6H_5NH_2)_8(SiF_4)_2 + 4NH_3 = (NH_3)_4(SiF_4)_2 + 3C_6H_5NH_2,$$

as was proved by its quantitative investigation.

2.8564 grams of trianiline disilicotetrafluoride yielded after treatment with ammonia 1.6240 grams of $(NH_3)_4(SiF_4)_2$.

	Calculated Percentage according to the Reaction given above.	Found.
$(NH_3)_4(SiF_4)_2$	56.67	56.85

When hydrochloric acid gas is passed over trianiline disilicotetrafluoride there is no action in the cold; but if the substance is gently warmed, complete decomposition sets in, aniline chloride sublimes along the tube in needles, and the hydrochloric acid contains fluoride of silicon, as was shown by passing it into water, when a precipitate of silicic acid was formed.

The action of ethyliodide was also tried. At 100° there was no action, but at 150° a product was formed which contained neither fluorine nor silicon, fluoride of silicon being given off when the tube was opened. Under these circumstances we did not think it worth while to try to purify the residual substance for analysis. Ethylbromide acted in the same way, but with more difficulty. Strong sulphuric acid decomposes trianiline disilicotetrafluoride, giving off fluoride of silicon. The action of the other common reagents with this substance could not be studied because it is decomposed by water or alcohol.

Dianiline silicotetrafluoride, $(C_6H_5NH_2)_4(SiF_4)_2$.—This substance was formed when aniline vapor was conducted into a receiver filled with fluoride of silicon, in the hope of preparing a compound containing a larger proportion of fluoride of silicon than that in the substance just described. The fact that, on the contrary, a body richer in aniline is formed, is probably to be accounted for by the high temperature at which the union of the two substances took place; and this view is confirmed by some experiments in which we heated the trianiline disilicotetrafluoride with one molecule of aniline to 150° in a sealed tube for about five hours: the product was a purplish mass, which gave results on analysis showing that a considerable quantity of aniline had been taken up, although not quite enough to convert the trianiline disilicotetrafluoride completely into the dianiline silicotetrafluoride. As the substance prepared directly from aniline and fluoride of silicon could not be purified on account of its slight stability, it was analysed in the crude state with the following results, which are as accurate as could be expected under these circumstances:

I. 0.3803 gram of the substance gave 0.0826 gram of silicic dioxide and 0.2255 gram of sodic fluoride.

II. 0.3032 gram of the substance gave 0.0645 gram of silicic dioxide and 0.1798 gram of sodic fluoride.

	Calculated for $(C_6H_5NH_2)_4(SiF_4)_2$.	Found. I.	II.
Silicon	9.65	10.14	9 93
Fluorine	26.20	26.83	26.85

Properties.—It is a white powder which cannot be sublimed, as it decomposes with blackening when heated. With water it is decomposed and dissolved, with deposition of silicic acid. It is possessed of but slight stability, as it gradually decomposes

spontaneously even when kept in a corked tube at ordinary temperatures, the substance turning yellow and giving up aniline, which was extracted with ligroine, and recognised by its smell and its characteristic color with bleaching powder, while the residue was pure trianiline disilicotetrafluoride, as shown by the following analyses:

I. 0.2370 gram of the substance gave 0.0578 gram of silicic dioxide and 0.1637 gram of sodic fluoride.

II. 0.1236 gram of the substance gave 0.0841 gram of sodic fluoride.

	Calculated for $(C_6H_5NH_2)_3(SiF_4)_2$.	Calculated for $(C_6H_5NH_2)_4(SiF_4)_3$.	Found. I.	Found. II.
Silicon	11.50	9.65	11.39	
Fluorine	31.24	26.20	31.25	30.79

In view of this decomposition of the dianiline silicotetrafluoride into aniline and trianiline disilicotetrafluoride, and also of the formation of the dianiline silicotetrafluoride by heating aniline with trianiline disilicotetrafluoride, there seems no doubt that the real formula of this substance is $(C_6H_5NH_2)_4(SiF_4)_3$, that is, double the simplest formula determined by analysis, and that the reaction for its spontaneous decomposition is the following:

$$(C_6H_5NH_2)_4(SiF_4)_3 = C_6H_5NH_2 + (C_6H_5NH_2)_3(SiF_4)_2.$$

Action of Fluoride of Silicon on other Bases.

Triorthotoluidine disilicotetrafluoride, $(C_7H_7NH_2)_3(SiF_4)_2$.—This substance was prepared by passing fluoride of silicon into a solution of orthotoluidine in benzol, when a very heavy gelatinous precipitate was formed, which was purified by washing with benzol and three sublimations. It can be formed also by the methods given under the aniline compound, but precipitation from a benzol solution gives the result more easily and furnishes a purer product. Its composition was determined by the following analyses:

I. 0.2100 gram of the substance gave 0.0476 gram of silicic dioxide.

II. 0.3530 gram of the substance gave 0.2177 gram of sodic fluoride.

III. 0.2330 gram of the substance gave 0.1440 gram of sodic fluoride.

IV. 0.2050 gram of the substance gave 0.1266 gram of sodic fluoride.

	Calculated for $(C_7H_7NH_2)_3(SiF_4)_2$.	Found. I.	II.	III.	IV.
Silicon	10.58	10.58			
Fluorine	28.73	...	27.90	27.97	27.94

Properties.—It is a white powder, subliming without melting or decomposition, like the corresponding aniline compound. It dissolves in hot common alcohol, and the solution deposits on cooling orthotoluidine fluosilicate in fine needles.

Triparatoluidine disilicotetrafluoride, $(C_7H_7NH_2)_3(SiF_4)_2$.—This substance was made and purified like the corresponding ortho compound, that is, by passing fluoride of silicon through a solution of paratoluidine in benzol, but even after four sublimations it had a distinct yellowish color. That the substance is essentially pure, however, in spite of this coloration, is shown by the following analyses:

I. 0.1928 gram of the substance gave 0.0438 gram of silicic dioxide.

II. 0.1472 gram of the substance gave 0.0922 gram of sodic fluoride.

	Calculated for $(C_7H_7NH_2)_3(SiF_4)_2$.	Found. I.	II.
Silicon	10.58	10.60	
Fluorine	28.73	...	28.34

In properties it resembles the corresponding ortho compound, but is decidedly less stable, showing a strong tendency to turn yellow on standing; and the paratoluidine fluosilicate deposited as the hot solution of the substance in alcohol cools, crystallises in thick needles.

Trimonochloraniline disilicotetrafluoride, $(C_6H_4ClNH_2)_3(SiF_4)_2$. This substance was made by passing fluoride of silicon over parachloraniline, and was purified by sublimation. Its composition was determined by the following analysis:

0.4807 gram of the substance gave 0.0990 gram of silicic dioxide and 0.2686 gram of sodic fluoride.

	Calculated for $(C_6H_4ClNH_2)_3(SiF_4)_2$.	Found.
Silicon	9.48	9.61
Fluorine	25.75	25.29

It resembles the corresponding aniline compound in its properties, and forms with hot alcohol a solution of the parachloraniline fluosilicate, which separates as the solution cools in beautiful long slender needles.

Parabromaniline forms a similar compound with fluoride of silicon, and gives with hot alcohol a solution depositing the parabromaniline fluosilicate in small pearly scales.

With *symmetrical tribromaniline* we could get no action, when we treated it with fluoride of silicon, the result of the experiment being negative, whether it was acted on alone in the solid state, or fused, or in solution in benzol. Symmetrical tribromaniline therefore does not combine with fluoride of silicon under the conditions which bring about the union with it of all the other bases studied.

Tridiphenylamine disilicotetrafluoride, $[(C_6H_5)_2NH]_3(SiF_4)_2$.—Solid pure diphenylamine is not acted on by fluoride of silicon; the statement made in a preliminary notice of this work, that a compound was formed under these conditions, was incorrect, the diphenylamine used for that first experiment being impure. If, however, fluoride of silicon is passed through a solution of diphenylamine in benzol, a white crystalline precipitate is deposited slowly, which was washed with benzol, dried at 100°, and analysed with the following results:

I. 0.4356 gram of the substance gave 0.0695 gram of silicic dioxide and 0.2141 gram of sodic fluoride.

II. 0.4192 gram of the substance gave 0.1986 gram of sodic fluoride.

	Calculated for $[(C_6H_5)_2NH]_3(SiF_4)_2$.	Found. I.	II.
Silicon	7.83	7.44	
Fluorine	21.26	22.23	21.43

Properties.—It forms thick white needles, which are decomposed by heat into fluoride of silicon and diphenylamine. When treated with water a precipitate of diphenylamine separates, and the filtrate contains fluosilicic acid. A quantitative study of the reaction gave the following results:

I. 0.8135 gram of the substance gave 0.5686 gram of diphenylamine and 0.3040 gram of potassic fluosilicate.

II. 0.4934 gram of the substance gave 0.3476 gram of diphenylamine.

In the calculated percentages given below it is assumed that all the diphenylamine is separated by the action of the water, and that four molecules of the compound will yield five of potassic fluosilicate, *i. e.* that the reaction with water is analogous to that of the corresponding aniline compound.

	Calculated.	Found. I.	Found. II.
Diphenylamine	70.91	69.89	70.44
Potassic fluosilicate	38.50	37.37	

If, as the numbers obtained seem to show, the reaction is similar to that of the trianiline disilicotetrafluoride with water, silicic acid should have been set free, but no trace of it could be discovered, the solution being free from any precipitate except the diphenylamine, and upon evaporation to dryness leaving no residue, while that silicic acid had not been carried down by the diphenylamine was shown by burning it and also by dissolving it in benzol. In neither case did it leave a residue. We have not been able to find any explanation for this curious observation, or to account for the formation of fluosilicic acid without the formation of silicic acid at the same time. That the soluble product was principally fluosilicic acid is proved by the fact that it gave a precipitate with potassic chloride.

Tridimethylaniline disilicotetrafluoride, $[C_6H_5N(CH_3)_2]_3(SiF_4)_2$.—Fluoride of silicon has no action on dimethylaniline alone, but, if the gas is passed through a solution of dimethylaniline in benzol, a flocculent precipitate is formed, which is gradually converted into a gummy mass that crystallises on standing. The crystals were purified by washing with benzol and ligroine, dried at 100°, and analysed.

0.1066 gram of the substance gave 0.0220 gram of silicic dioxide and 0.0584 gram of sodic fluoride.

	Calculated for $[C_6H_5N(CH_3)_2]_3(SiF_4)_2$.	Found.
Silicon	9.81	9.63
Fluorine	26.62	24.77

The number for the fluorine is far from satisfactory, which is accounted for by the difficulty of purifying this decidedly unmanageable substance. It is, however, near enough to show that the substance can have no other composition than that assigned to it by us.

Properties.—It forms an indistinct crystalline mass, which is decomposed by heat, and gives no stable fluosilicate, when treated with alcohol.

Trichinoline disilicotetrafluoride, $(C_9H_7N)_3(SiF_4)_2$.—Chinoline alone is not acted on by fluoride of silicon; but, if the gas is passed

through a solution of chinoline in benzol, a gummy precipitate is formed at first, which becomes gradually converted into needle-shaped crystals. The product was purified by washing with benzol or ligroine, and dried at 100°. The same substance is obtained when chinoline fluosilicate is sublimed, and the analysis numbered II is of a preparation made in this way.

I. 0.1634 gram of the substance gave 0.0323 gram of silicic dioxide.

II. 0.0730 gram of the substance gave 0.0404 gram of sodic fluoride.

	Calculated for $(C_9H_7N)_3(SiF_4)_2$.	Found. I.	II.
Silicon	9.41	9.23	
Fluorine	25.55	...	25.01

Properties.—It crystallises in needles, and sublimes without melting or decomposition. Although hot alcohol usually decomposes it, as described below, on one occasion it dissolved it without decomposition, and this solution gave on cooling thick needles, which gave the following results on analysis:

0.0903 gram of the substance gave 0.0176 gram of silicic dioxide and 0.0506 gram of sodic fluoride.

	Calculated for $(C_9H_7N)_3(SiF_4)_2$.	Found.
Silicon	9.41	9.10
Fluorine	25.55	25.38

On addition of water the substance analysed was decomposed with deposition of silicic acid. We have not succeeded, however, in repeating this experiment, as in all other cases the product from the action of hot alcohol has been chinoline fluosilicate, which crystallises in long thick needles as the solution cools, and gives a clear solution with water. Its composition was determined by the following analyses of the substance purified by two crystallisations:

I. 0.1244 gram of the substance gave 0.0200 gram of silicic dioxide.

II. 0.2054 gram of the substance gave 0.0325 gram of silicic dioxide and 0.1254 gram of sodic fluoride.

	Calculated for $(C_9H_7N)_2H_2SiF_6$.	Found. I.	II.
Silicon	6.96	7.50	7.38
Fluorine	28.35	...	27.64

The trichinoline disilicotetrafluoride resembles the corresponding aniline compound closely in its properties.

Didimethylamine silicotetrafluoride, $[(CH_3)_2NH]_4(SiF_4)_2$.—When dry dimethylamine (prepared according to Baeyer and Caro) was mixed with fluoride of silicon, a white powder was deposited, which was analysed in the crude state, since it could not be purified because of its very slight stability.

0.2320 gram of the substance gave 0.0740 gram of silicic dioxide and 0.2038 gram of sodic fluoride.

	Calculated for $[(CH_3)_2NH]_4(SiF_4)_2$.	Found.
Silicon	14.43	14.89
Fluorine	39.17	39.75

Properties.—A white solid, which, like the corresponding compound of aniline, is very unstable, decomposing spontaneously at ordinary temperatures into dimethylamine and the following compound—a decomposition which is hastened by heat.

Tridimethylamine disilicotetrafluoride, $[(CH_3)_2NH]_3(SiF_4)_2$.—This substance was made by subliming the compound just described, when dimethylamine was given off as a secondary product. It was purified by a second sublimation, and its composition determined by the following analyses:

I. 0.1871 gram of the substance gave 0.0660 gram of silicic dioxide.

II. 0.2800 gram of the substance gave 0.0960 gram of silicic dioxide and 0.2694 gram of sodic fluoride.

	Calculated for $[(CH_3)_2NH]_3(SiF_4)_2$.	Found.	
		I.	II.
Silicon	16.33	16.46	16.00
Fluorine	44.31	...	43.53

Properties.—It is a white powder, resembling the corresponding aniline compound in appearance and behavior when heated, although it sublimes at a higher temperature. It also differs from the aniline compound in being deliquescent.

Finally, we may add the following experiments, which gave products of so little promise that we did not attempt to analyse them, but which show that fluoride of silicon acts also on alkaloids, and on amides which can form salts.

Furfurine, when treated in benzol solution with fluoride of silicon, gave a gummy mass similar to that obtained from dimethylaniline, which, however, did not crystallise on standing.

Dry powdered *urea* was converted by fluoride of silicon into a pasty mass, which was decomposed with evolution of ammonia when the attempt was made to sublime it. The sublimate contained fluorine and silicon, but we did not continue the study of it, as we had no guaranty that it was a homogeneous substance.

Constitution of the Silicotetrafluorides.

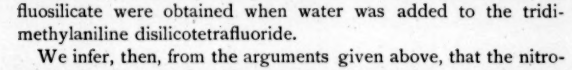
Although we have not succeeded in obtaining an absolute direct proof of the constitution of the substances described in this paper, we have been able to reduce the possible formulas that can be assigned to them to a very small number by the following course of reasoning. In the first place, we assume that all the substances described in this paper, which contain three molecules of the base combined with two of fluoride of silicon, have the same constitution; an assumption which is justified by the fact that they are all made by the direct addition of fluoride of silicon to the base, and also by the strong resemblance in their properties, the differences observed being such as might well occur among substances belonging to the same class.

Upon considering, in general, the way in which the fluoride of silicon could attach itself to a base, we have been able to find only three probable methods, which we will proceed to discuss as applied to our compounds. (*a.*) By replacing the hydrogen of the amido group, forming a substance which would be at once an anilid and a fluosilicate. This method would seem at first sight the most probable, especially since A. Harden[1] has found that chloride of silicon gives with aniline $SiCl_2(NHC_6H_5)_2$ and aniline chloride; but this mode of union is impossible, since both chinoline and dimethylaniline, which contain no hydrogen attached to their nitrogen, form compounds of this class. (*b.*) By the action of the fluoride of silicon on the benzol ring, forming a substance analogous to pararosaniline fluosilicate. This hypothesis, which is improbable on account of the ease with which the substances are broken up by water, is rendered entirely inadmissible by the formation of the dimethylamine compound, which contains no ring. (*c.*) On the supposition that the fluoride of silicon combines with the base to form a sort of salt, this view is the only one compatible with our results, and its correctness is confirmed by the observation that all the substances tried formed salts, with one

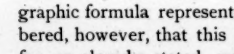
[1] J. Lond. Chem. Soc. 1887, 1, 40.

exception, tribromaniline, and that this was the only one which did not form a silicotetrafluoride; further, the stability of the silicotetrafluorides keeps pace with the stability of the salts of the bases; those like aniline, the two toluidines, parachloraniline, chinoline, and dimethylamine, which form stable salts, giving silicotetrafluorides which can be sublimed without decomposition, whereas diphenylamine and dimethylaniline gave compounds decomposed by heat. That the salts of diphenylamine are unstable, being decomposed by water, is well known, and although we have not been able to find any published statement about the salts of dimethylaniline that would imply they are unstable, our own work has furnished the proof that the fluosilicate at least is less stable than that of aniline, as only the products of the decomposition of the fluosilicate were obtained when water was added to the tridimethylaniline disilicotetrafluoride.

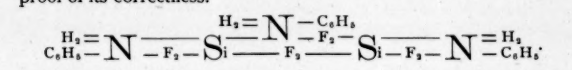
We infer, then, from the arguments given above, that the nitrogen in the silicotetrafluorides is in the quinquivalent condition, and think it most probable that one of the two additional bonds is satisfied by silicon, the other by fluorine, and that the following graphic formula represents its constitution. It should be remembered, however, that this formula is only the most probable one, for, as already stated, we have been able to bring no absolute proof of its correctness.



If this formula is adopted, the formation of the silicotetrafluorides can be explained in the following way. In the first place one molecule of the fluoride of silicon acts upon one molecule of the base to give the group



and, although this mode of union seems strange at first sight, it is not without analogy, if we consider the close relationship of silicon and carbon, as then it is similar to the formation of ammonium salts by the action of methyliodide on a base, as shown by the following reactions:



Since the group

$$\begin{matrix} H_2 = \\ C_6H_5 - \end{matrix} N \begin{matrix} - SiF_3 \\ - F \end{matrix}$$

is at once a fluoride and a substituted fluoride of silicon, an action next takes place similar to the formation of a fluosilicate from a fluoride and fluoride of silicon, thus:

$$\begin{matrix} H_2 = \\ C_6H_5 - \end{matrix} N \begin{matrix} - SiF_3 \\ - F \end{matrix} = \begin{matrix} H_2 = \\ C_6H_5 - \end{matrix} N \begin{matrix} \overline{\qquad\qquad} \\ - F = F - \end{matrix} Si = F_2;$$

$$2KF + SiF_4 = \begin{matrix} K - F = F - \\ K - F = F - \end{matrix} Si = F_2.$$

In this reaction the formation is assumed of the bivalent radical F_2^{II}, which has been proved to exist in hydrofluoric acid by Mallet's determination[1] of the vapor density leading to the formula H_2F_2, and the assumption of the presence of which in fluosilicic acid explains its relation to silicic acid in the most satisfactory way. The substance

$$\begin{matrix} H_2 = \\ C_6H_5 - \end{matrix} N \begin{matrix} \overline{\qquad} \\ - F_2 - \end{matrix} Si = F_2$$

next acts on another molecule of the base in the same way that the fluoride of silicon did originally, forming

$$\begin{matrix} H_2 = \\ C_6H_5 - \end{matrix} N \begin{matrix} \overline{\qquad} \\ - F_2 - \end{matrix} Si \begin{matrix} = \\ - F \end{matrix} N \begin{matrix} - C_6H_5 \\ - F \end{matrix};$$

but it would seem that the acid nature of the silicon has been so weakened by the introduction of two aniline molecules, that the atom of fluorine left attached to the silicon cannot combine with the fluorine attached to the nitrogen, and therefore this latter is saturated by the more acid fluorine of a fluoride of silicon carrying only one aniline molecule, thus:

$$\begin{matrix} H_2 = \\ C_6H_5 - \end{matrix} N \begin{matrix} \overline{\qquad} \\ - F_2 - \end{matrix} Si \begin{matrix} = \\ - F \end{matrix} N \begin{matrix} - C_6H_5 \\ - F \end{matrix} + \begin{matrix} F - \\ F - \end{matrix} Si \begin{matrix} \overline{\qquad} \\ - F_2 - \end{matrix} N \begin{matrix} = H_2 \\ - C_6H_5 \end{matrix}$$

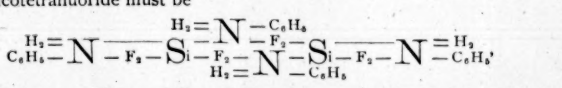
$$= \begin{matrix} H_2 = \\ C_6H_5 - \end{matrix} N \begin{matrix} \overline{\qquad} \\ - F_2 - \end{matrix} Si \begin{matrix} = \\ - F \end{matrix} N \begin{matrix} - C_6H_5 \\ - F_2 - \\ F - \end{matrix} Si \begin{matrix} \overline{\qquad} \\ - F_2 - \end{matrix} N \begin{matrix} = H_2 \\ - C_6H_5 \end{matrix}.$$

If, then, the two atoms of fluorine remaining attached simply to silicon are united, the formula given above is constructed. Our only reason for joining these last atoms of fluorine is that it makes the molecule more symmetrical, but it is also possible that they remain univalent.

Turning next to the compounds formed by the union of the base

[1] This Journal **3**, 189.

and fluoride of silicon in the proportion of two molecules of the former to one of the latter; as has been already argued, it is necessary to double the simplest formula which can be assigned to these substances, because they break up into the free base and the compound of three molecules of the base to two of fluoride of silicon, and also because they can be formed by a reaction the reverse of this decomposition. If, then, the formula discussed above is given to the trianiline disilicotetrafluoride, the formula of the dianiline silicotetrafluoride must be



and the very slight stability of the substance can be explained by the neutralisation of the acid properties of the silicon and fluorine, already alluded to, by the introduction of so many molecules of base, which makes them hold the last molecule of the base with comparatively little force. On the other hand, we have not been able to find any explanation for the stability of the compound derived from ammonia, as the only one we could think of—viz. that the ammonia being a stronger base than aniline would attach itself more firmly to the slightly acid molecule—is rendered inadmissible by the slight stability of the compound made from dimethylamine, a base nearly, if not quite, as strong as ammonia itself. It is possible that the ammonia compound has an entirely different constitution from the compounds of the organic bases, but we have no experimental material for testing the correctness of this hypothesis except Mixter's determination[1] of the vapor density of this substance, which showed that it was dissociated into four volumes of ammonia and two of fluoride of silicon, and therefore that the simplest formula of the ammonia compound must be doubled, which would look as if it had a constitution similar to the organic compounds.

We may add that Harden[2] obtained by the action of chloride of silicon on pyridine, or chinoline compounds $(C_5H_5N)_2SiCl_4$, and $(C_9H_7N)_2SiCl_4$; but as they give up chloride of silicon spontaneously, it is probable that they are not analogous in constitution to our substances.

The study of the action of fluoride of silicon on organic bases will be continued by one of us in this laboratory.

[1] This Journal **2**, 153.

[2] J. Lond. Chem. Soc. 1887, **1**, 40.

LVI.—A DETERMINATION OF THE RELATION OF THE ATOMIC WEIGHTS OF COPPER AND SILVER.

By Theodore W. Richards.

In the Report of the Committee on Electrolysis made to the British Association at Birmingham, of which an advance copy has been received by Professor Cooke through the kindness of Dr. Oliver Lodge, a direct determination is given of the ratio between the atomic weight of copper and that of silver, based on the electrolytic experiments of W. N. Shaw. As the value of the ratio thus obtained is quite different from that usually accepted, it seemed to Professor Cooke desirable that the results should be confirmed by a direct chemical method, and the writer was intrusted with this investigation.

Of the work worthy of consideration which has thus far been done upon the atomic weight of copper, first in chronological order comes that of Berzelius,[1] who made two determinations of the weight of copper formed by the reduction of pure cupric oxide by hydrogen. He found the percentage of copper in this compound to be $79.823 \pm .002$. This corresponds to an atomic weight of 63.153, taking oxygen $= 15.963$, with Clarke. The next determination was by Erdmann and Marchand,[2] who used the same method. They found the percentage of copper in cupric oxide to be $79.8645 \pm .0038$ as a mean of four determinations—a value which makes $Cu = 63.316$. Millon and Commaille,[3] in three determinations—which did not, however, closely agree with one another—found the relation $CuO : Cu = 100 : 79.7787$; and calculating from this relation the atomic weight of copper, the value 62.979 is obtained. Dumas[4] made several determinations of the reduction of cupric oxide and the synthesis of cuprous sulphide, and calculates the value $Cu = 63.5$.

Hampe,[5] whose work gave the most concordant results thus far secured, obtained from three determinations of the percentage of copper in cupric oxide the mean value of $79.8347 \pm .0013$; and from two analyses of anhydrous cupric sulphate by electrolytic precipitation he found the proportion $CuSO_4 : Cu = 100 : 39.725 \pm .0007$. The atomic weights of copper from these two methods are respectively 63.197 and 63.173.

[1] Poggend. Annal. **8**, 177.
[2] J. prakt. Chem. **31**, 389 (1844).
[3] Ztschr. anal. Chem. **2**, 475 (1863).
[4] Ann. chim. phys. (3) **55**, 129.
[5] Ztschr. anal. Chem. **13**, 352 (1874).

This was in 1874; and the subject has rested undisturbed until last year, when W. N. Shaw, in the paper before referred to, sought to prove the accuracy of Faraday's law of electrolysis in atomic proportions, by means of the actual weights of silver and copper deposited in cells in the same circuit. For the particulars of his method the Report of the Committee on Electrolysis should be consulted; it is sufficient here to say that as the mean of many determinations he finds the ratio of the silver and copper precipitated to be 3.39983 : 1. Correcting this result for variations in current density, he obtains the value 3.39888, and finally adopts the practically identical value 3.400, which makes the ratio Ag : Cu = 17 : 10. This last value makes Cu = 63.333, while the corrected value gives as the atomic weight the quantity 63.360.

Below is a summary of all the results:

Berzelius, from CuO	63.153
Erdmann and Marchand, from CuO	63.316
Millon and Commaille, from CuO	62.979
Dumas, from CuO and Cu_2S	63.5
Hampe, from CuO	63.197
" from $CuSO_4$	63.173
W. N. Shaw, by relation to silver	63.333
" " " corrected	63.360

The most obvious chemical method for the determination of the relation of the atomic weights of silver and copper is by the precipitation of silver from a solution of a pure silver salt by means of pure copper; and this was the method adopted in the present determination. Hampe, in his work on the atomic weight of copper, attempted the same method, but rejected it for two reasons—the first being that the silver dissolved, or appeared to dissolve, to a slight extent in the hot water used for washing; and the second being that it was impossible to prevent copper from coming down with the silver, no matter how long the precipitate was digested with the argentic nitrate solution. As will be seen, however, both of these difficulties have been entirely overcome.

The silver salt selected for the precipitation was the nitrate, on account of its ready crystallisation, its easy solubility in water, and the facility with which it can be obtained pure. For the preparation of the salt used in the work, ordinary pure argentic nitrate was crystallised many times from hot water, and finally fused for

two hours in an air-bath kept at 205° C.—a few degrees above its melting point. This preparation was a white translucent substance interspersed with transparent crystals, dissolving completely in water, and giving a colorless solution which was wholly neutral.

The copper used was prepared by electrolysis from cupric sulphate, through the kindness of Mr. Wilson, of the University Press. It was cut into small pieces, and these were digested in succession with weak potassic hydrate, dilute sulphuric acid, and then a very large amount of water. The copper was then boiled with water for about half an hour and washed with a large amount of distilled water, then dried and reduced at a low red heat by means of perfectly pure hydrogen, and allowed to cool in a stream of the gas. The metal thus prepared had a beautiful red metallic lustre, and showed no trace of oxidation after keeping a month. Before use it was dried in an air-bath at 110°, allowed to cool in a desiccator, and weighed by itself on a balance which was distinctly sensible to a twentieth of a milligram. In addition to receiving the treatment described above, the copper used in the fifth and sixth experiments was oxidised in a stream of pure air for half an hour, and then again reduced by hydrogen; but the concordance of those two results with the others shows that this precaution was not necessary.

In a few preliminary experiments it was found that on the temperature of the solution, and on the temperature alone, depended the regularity with which the silver was precipitated by the copper. At 90° the deposition is very rapid, nitrous fumes are evolved, and a large amount of copper comes down with the silver. As the temperature of the solutions used is lower, the reaction becomes less rapid, and the amount of copper deposited with the silver less, until at ordinary temperatures it is comparatively small; and below 0° the silver comes down absolutely pure, and not the least evolution of gas is observed. One of the difficulties of Hampe can then be overcome by keeping the beaker containing the solution in a freezing mixture; and the perfect definiteness of the reaction, which before might have been questioned, is thus established. The duration of the reaction at —1° is from twelve to twenty-four hours, according to the dilution of the argentic nitrate. The more dilute the solution is, the longer the precipitation takes, and the more finely divided is the deposited silver; but when the solution is very concentrated, the reaction is completed in a comparatively short time, and the silver comes down in a beautiful compact crystalline crust which takes the form of the copper.

The silver which was formed was collected in a Gooch crucible and washed with cold water, of which less than 250 cc. were necessary to give a filtrate in which no trace of silver or copper could be detected.

The fact that the determinations given below agree so exactly with each other is of itself proof that no silver was dissolved—first, because the precipitate in the different experiments was of very different degrees of fineness; and secondly, because the precipitate in each experiment was washed with a different amount of water, the silver of the last experiment having at least four times as much water passed over it as that of the first. And the fact that the results are not affected by either circumstance shows clearly that no perceptible amount of silver could have been dissolved; for if so, the loss must have varied both with the condition of the precipitate and with the amount of the wash water. The different result obtained by Hampe was probably the effect of hot water on a very finely divided precipitate.

The silver, whether in crystalline plates or in crystalline powder, formed a very convenient precipitate with which to work; it was easily transferred and easily washed, did not adhere to the glass, and was in every way adapted for quantitative work.

The conditions of the following experiments as regards the quantity of water and the excess of argentic nitrate used above the amount required to dissolve the copper, were varied as much as possible. In some determinations barely enough of the argentic nitrate was used to effect the solution, while in others the excess of the silver salt amounted to nearly two grams. The time allowed the reactions was also varied from twenty-four to seventy-two hours.

Relation of Silver to Copper.

No. of Expt.	cc. H_2O used.	Weight Cu taken.	Weight Ag formed.	Equivalent $Ag_2 : Cu = 1 : n$.	Atomic Weight Cu Ag = 108.	Ag = 107.675.
1	20	0.53875	1.8292	0.29452	63.618	63.427
2	25	0.56190	1.9076	0.29456	63.624	63.432
3	120	1.00220	3.4016	0.29462	63.639	63.447
4	30	1.30135	4.4173	0.29462	63.638	63.447
5	20	0.99870	3.39035	0.29457	63.628	63.437
6	25	1.02050	3.4646	0.29456	63.623	63.434
			Average,	0.29457	63.628	63.437

The mean value, 63.437, has a greatest variation of ± .01 and a probable error of ± .0023.

The value obtained by Shaw was	63.333
" " " " corrected . . .	63.360
The value given by Clarke is	63.173

It remains only to prove the absolute purity of the copper used and the silver formed. The only metals which could affect the atomic weight of copper to an appreciable extent, if present in traces, are bismuth and silver. The former was tested for with great care, using a delicate spectroscope, and not the faintest trace of the very well-defined blue bismuth line was apparent; further, ten grams of the copper were dissolved in nitric acid, a little potassic hydrate added to the diluted solution, and the whole boiled and shaken for three hours. According to Hampe, all the bismuth present will be found in the basic precipitate; this was tested qualitatively for the metal, and not a trace was found. The solution of a portion of the copper in pure nitric acid gave not the faintest trace of opalescence with hydrobromic acid, excess of ammonic hydrate, or baric chloride. A gram of the copper was tested for arsenic and antimony in a Marsh-Berzelius apparatus, and no trace of a mirror was obtained. As the presence of so much copper would cause the generator to run too rapidly, the solution was treated with just enough potassic ferrocyanide to effect precipitation, and the colorless filtrate was run into the apparatus. This method has been found to give good results. The copper and the precipitated silver each dissolves in nitric acid without leaving a trace of residue.

If the copper is pure, the only possible impurity which the silver could contain is copper; and this was tested for with great care in each precipitate by dissolving one to two grams in nitric acid and adding excess of ammonic hydrate. In no case was the slightest blue color noticed; and as under the same circumstances a tenth of a milligram of copper gave a distinct bluish tinge, it may be assumed that the silver contained no copper. This method is a convenient one for the preparation of chemically pure silver, and avoids the necessity of fusion and the concomitant absorption of oxygen and possible admixture of silicic anhydride.

Although the value of the atomic weight of copper obtained, 63.44, does not exactly coincide with Shaw's results, it is at least

very much nearer to them than is the old accepted value of 63.17; especially if we take his result as corrected for current density. The new value is very nearly that found by Dumas from cuprous sulphide, and it falls within the limits assigned by L. Meyer and Seubert as the possible error of the accepted value.

LVII.—FURTHER INVESTIGATION ON THE ATOMIC WEIGHT OF COPPER.

By Theodore William Richards.

After the investigation described in the preceding article was completed, it became necessary, in the course of some further experiments, to ignite a portion of the silver from determination No. 5 of that series, and it was found that two grams of silver lost four tenths of a milligram by this process. It is thus evident that 150° is not a temperature high enough to drive out all the water from the silver, and hence the results before given are incorrect by a slight amount. In this determination the weight of the silver was 3.39035 grams after drying at 150°, hence its weight after ignition would have been 3.38975 grams. The weight of copper taken was .9987 gram, therefore the corrected atomic weight of copper would be 63.452 instead of 63.437.

Unfortunately, all the silver formed in the other determinations had been employed in testing for the presence of copper; hence it was impossible to determine whether the other samples would lose water on heating in a similar manner. It seemed, therefore, desirable to make a new series, using samples of pure copper prepared from the ores of different localities. Should the result be the same in each instance we should have a very strong proof, not only that the copper used in each case was pure—because the different samples would probably contain different impurities—but also that the atomic weight of copper is a perfectly constant quantity.

The method used was exactly that of the previous paper, although more difficulty was found in keeping the solution below zero for twenty-four hours than was the case before, because of the warmer weather. Several determinations had to be rejected because the temperature rose above zero and copper was precipitated with the silver. Upon splitting open the fine crystalline plates of silver precipitated in these rejected experiments, a light

green precipitate of basic cupric nitrate was found adhering to the inner surface, which could not be removed by continued washing with cold water. The presence of this precipitate explains the admixture of copper with the silver precipitated above zero, and points at once to the mechanism of the chemical action.

When copper is placed in a solution of argentic nitrate, two reactions take place, and the temperature regulates the predominance of one or the other. The chief reaction is the simple one ordinarily written; it alone is active between 0° and —5°, and it is the chief one even at 100°. The secondary reaction, which is active at 100°, but which entirely ceases below 0°, may perhaps be written thus—assuming that the basic nitrate has the formula usually assigned to it:

$$4AgNO_3 + 4Cu + 3H_2O =$$
$$Cu(NO_3)_2 . 3Cu(OH)_2 + 2Ag_2 + NO + NO_2.$$

Evidently in this reaction the copper precipitates only one half of its equivalent of silver. It will be remembered that an evolution of nitrous fumes was previously observed when the temperature rose above the freezing point.

The argentic nitrate used in the new series was prepared as before, except that even greater precautions were taken to insure its purity, by successive crystallisations and fusions.

Two samples of copper were used, one from Lake Superior, the other from Germany. For the purification of the former the sample was dissolved in sulphuric acid, with the addition of nitric acid; the solution was evaporated to dryness, and the solid heated over asbestos in a porcelain dish, until the fumes of sulphuric acid ceased coming off. The cupric sulphate was now dissolved in water, crystallised twice, and the diluted solution of the last crystals boiled and shaken with a little potassic hydrate for three hours. The solution was now filtered, and the cupric sulphate was crystallised several times from hot water. Finally, the solution of the last pure crystals, strongly acidified by sulphuric and a little nitric acid, was decomposed by the current of a Bunsen cell, and the chemically pure copper deposited on thick platinum foil.

The second sample of copper was prepared from German cupric oxide in a similar manner, except that the sulphate was crystallised a greater number of times. In this connection it may be mentioned that, of many samples of German cupric oxide tested, not one was found that did not contain a comparatively large amount of arsenic.

In the case of many samples, after several reductions with pure hydrogen and oxidations, the arsenic will actually sublime off as arsenious oxide; and a quantity of the substance was collected in this manner.

The method of cleaning the copper was similar to that previously adopted; it was treated in succession with dilute potassic hydrate, dilute sulphuric acid, and a very large amount of water, and then dried and reduced by pure hydrogen.

The silver which was obtained by precipitation from the pure argentic nitrate was first washed and dried at 150°, and weighed, as before; and was then heated to incipient redness, and weighed again. The loss of weight by this process varied with the different samples between three tenths of a milligram and one milligram. The Gooch crucible and asbestos mat subjected to the same treatment did not lose an appreciable quantity. The results were calculated for the weight of silver both before and after ignition, and it will be noticed that the first column of results corresponds almost exactly to the results given in the previous paper. The silver was in each case tested for copper, and no trace was found.

Results.

German Copper.

No. of Experiment.	Weight Cu.	Weight of Silver formed.		Cu : Ag_2 = 1 : *n*.	Atomic Weight Cu (Ag = 107.675).	
		Before Ignition.	After Ignition.		Before Ignition.	After Ignition.
	Grams.	Grams.	Grams.			
1	0.75760	2.5723	2.5713	3.3940	63.426	63.450
2	0.95040	3.2261	3.2256	3.3939	63.440	63.451
3	0.75993	2.5798	2.5794	3.3942	63.438	63.447

Average, 63.449

Greatest variation = ± .002. Probable error = ± .0010.

Lake Superior Copper.

No. of Experiment.	Weight Cu.	Weight Ag formed.		Cu : Ag_2 = 1 : *n*.	Atomic Weight Cu (Ag = 107.675).	
		Before Ignition.	After Ignition.		Before Ignition.	After Ignition.
	Grams.	Grams.	Grams.			
4	1.02060	3.4650	3.4640	3.3942	63.432	63.448
5	0.90460	3.0705	3.0701	3.3939	63.444	63.452

Average, 63.450

Greatest variation = ± .002. Probable error = ± .0013.

The average of these two series is 63.450, with greatest variations of +.002 and —.003, and a probable error of ±.0006. The average of the results calculated from the weight of silver dried at 150° is 63.436, while the results published in the preceding paper gave 63.437.

The complete concordance of these results with each other and with the previous value above referred to, would point strongly to the following conclusions.

First, that the copper used in each case was absolutely free from metallic alloy; for manifestly the three entirely different samples would be likely to contain different impurities, or at least different amounts of the same impurity. The copper was tested for sulphur with the greatest care by solution in nitric acid and treatment with baric chloride, and no trace of cloudiness was perceptible. That the copper was *absolutely* free from impurity is not contended; only that it did not contain a weighable amount of impurity in one gram, the amount used in each experiment. It is manifest that attempts to purify the copper beyond this limit would be labor thrown away and would produce no effect upon the atomic weight. For example, one tenth of a milligram is a very large amount of foreign material to suppose existing in a gram of copper purified with such care; but this large amount would only change the atomic weight five units in the third decimal place, a quantity which is of no consequence when the atomic weight is in doubt three units in the first decimal place.

Another and still more positive conclusion reached by these results is that the atomic weight of copper is a constant quantity with reference to nitric acid and silver. If copper had a variable atomic weight, it would surely appear in specimens taken from such widely different sources. This conclusion still remains in force even supposing there be a constant error in the process, for the constant error must affect all the results equally, and could not possibly equalise unlike results.

A third conclusion pointed out by the determinations is that the argentic nitrate was the normal compound and quite pure; for it will be remembered that two entirely different samples had been used in the course of the work.

There is but one point which remains to be considered, and that is the existence or non-existence of a constant error in the reaction. That this is by far the most important point in the whole dis-

cussion it is unnecessary to state. Whether there be such a constant error, future investigations may show; for the present it is sufficient to say that it is extremely difficult to see where such an error might creep in. The whole reaction is so simple and so sharp that the probability of error is reduced to a minimum, and in every case any possible cause of error has been guarded against.

Professor Cooke, under whose direction the whole investigation has been conducted, suggested that similar experiments be made, using argentic sulphate instead of the nitrate; but after a large number of trials this was found to be impracticable: first, because the solution has a much higher freezing point than that of the nitrate; and secondly, because the solution was necessarily so dilute, on account of the slight solubility of argentic sulphate, that the complete precipitation of the silver required a much longer time, giving more opportunity for secondary reactions. The silver was always accompanied by a very slight admixture of some basic cupric sulphate; and hence this method, which, if successful, would have been able to throw much light on the question of a constant error in the previous results, had to be abandoned.

CAMBRIDGE, *December* 15, 1887.

LVIII.—ADDITIONAL NOTE ON THE RELATIVE VALUES OF THE ATOMIC WEIGHTS OF HYDROGEN AND OXYGEN.[1]

BY JOSIAH PARSONS COOKE AND THEODORE WILLIAM RICHARDS.

The preceding paper[2] on this subject was already in print, and a number of the extra copies had been distributed, when the writer received a letter from Lord Rayleigh, stating that he had been engaged on a similar work, and had observed that the glass balloon used in Regnault's method of weighing gas volumes, when exhausted, was sensibly condensed by the pressure of the air. Obviously, if this were true, the *tare* of the balloon thus exhausted would be too large in consequence of the lessened buoyancy of the atmosphere, and hence the subsequently observed weight of gas when the balloon was filled would be too small. A shrinkage amounting to a single cubic centimeter would make a difference of

[1] Communicated by the authors, from the Proceedings of the American Academy of Arts and Sciences.

[2] This Journal **10**, 81; and Proceedings American Academy of Arts and Sciences.

about 1.29 milligrams, and Lord Rayleigh suggested that our results might have been influenced by a constant error arising from this source. As the same balloon represented in Figure 1 of the preceding paper had been used in all our determinations, and was still in good condition, there was no difficulty in determining the amount of shrinkage under exhaustion, and thus finding the correction which ought to be applied to the results on this account. The method we used was briefly as follows:

The balloon was first exhausted, and then completely filled with boiled distilled water at an observed temperature. The weight of this water having been taken, and the internal volume of the balloon thus determined, a small portion of the water—190 cubic centimeters—was run out, and the volume estimated both by direct measurement and also by reweighing the balloon. With these data we could readily calculate the volume of air left in the balloon for any given temperature, and the small amount of water lost by evaporation in the subsequent exhaustion produced no sensible effect on the result, as a knowledge of the volume within five cubic centimeters was all that the present problem required, and the water did not lose in weight more than two grams during the whole series of experiments.

The balloon was now thoroughly exhausted, allowed to stand, and again exhausted several times, until a vacuum gauge connected with it remained constant over night, and indicated the calculated tension of aqueous vapor, which showed that all the air—dissolved or otherwise—had been practically removed.

A sufficient mass of water was left in the balloon to sink it under water, and thus immersed in a large vessel filled with distilled water (which had been boiled and allowed to cool), it was now suspended from the beam of the balance used throughout this investigation. No air bubbles formed on the glass, and care was taken to remove all entangled air from the connecting tubes. The weight soon became constant, and the tare could be accurately determined within a centigram. The connecting tubes of the balloon were next lifted above the surface of the water, and, after carefully drying the inlet, the outside air was admitted, and the temperature of the water in the tank and the height of the barometer observed. On again immersing the balloon there was a large loss of weight—about 1.4 grams—over six times the weight of air admitted—only about 0.2 gram. There had evidently been a marked shrinkage

under exhaustion amounting to about 1.6 cubic centimeters. This decrease of weight was noted after the equilibrium had become constant, usually in about five minutes.

It is probable that the admitted air was saturated with moisture, and the calculation is based upon that assumption; but this would make no practical difference in the weight so far as the problem before us is concerned. Appended is an example of the method.

SERIES I. *Determination* 2.

Tare of globe exhausted = 198.22 grams. T° = 17.30°.
" " filled = 196.83 T° = 17.30°.

Observed loss of weight = 1.39

Atmospheric pressure = 75.86 cm.
Tension of aqueous vapor = 1.46

Difference = 74.40

Weight of 188 cc. moist air at 17.3° and 74.4 cm. = .22 gram.
Observed loss of weight of globe = 1.39

Water displaced by difference of volume = 1.61

Diff. of volume corresponding to 74.4 cm. pressure = 1.61 cc.
" " " 76.8 cm.[1] " = 1.66 cc.
Weight of 1.66 cc. of air at 76 cm. and 22° C.[1] = 1.98 mg.

Below are given the data of the two series of determinations which were made:

SERIES I.

Number.	Loss of Weight. Grams.	Atmospheric Pressure. Centimeters.	Temperature. °C.	Correction. Milligrams.
1.	1.34	76.40	18.10	1.92
2.	1.39	75.86	17.30	1.98
3.	1.39	75.80	17.32	1.98
4.	1.37	75.78	17.40	1.96
5.	1.39	75.75	17.45	1.99
				1.97

[1] 22° C. and 76 cm. pressure were the average atmospheric conditions at the times of weighing the globe in the previous determinations, and 76.8 cm. was the average difference of the pressure on the globe when exhausted and full of hydrogen.

SERIES II.

6.	1.38	75.60	14.50	1.98
7.	1.39	75.60	14.50	2.00
8.	1.39	75.58	14.60	1.99
9.	1.40	75.58	14.61	2.01
10.	1.39	75.58	14.65	1.99
				1.99

Total average, 1.98 milligrams.

The quantity 1.98 milligrams is then the correction sought, and this closely agrees with Lord Rayleigh's estimate of the value in the letter above referred to. Since in the work described in the preceding paper all the data required for the calculation were not recorded in every case, it will be impossible to apply this correction to each determination separately. But no sensible error can result if we add the correction to the average apparent weight of the hydrogen, easily calculated from the data given in the table on page 107.

The total weight of the hydrogen burnt in the sixteen determinations as observed was 6.7029 grams. Add to this sixteen times the correction, or $16 \times 0.00198 = 0.0317$, and we obtain 6.7346 grams for the corrected weight. The total weight of the water formed was 60.1687 grams. Hence we find by difference for the total weight of oxygen consumed in the combustions 53.4341 grams; and the corrected atomic weight of oxygen is $2(53.4341 \div 6.7346) = 15.869$.

The probable error of this result is no greater than that of the "Total average" given on page 107; for the value of the constant correction must be certainly known within the one fiftieth of a milligram. It is true that there are several variable elements which enter into the determination of this value, but they can all be estimated with far greater accuracy than the conditions of our problem require. We may therefore write as the present result of our work, $H : O = 1.000 : 15.869$.

Atomic weight of oxygen, 15.869 ± 0.0017.

If we compare this result with that of Dumas, as before, on page 109, we have for the complete analysis of water:

Percentage of oxygen after Dumas . . .	88.864 ± 0.0044
Percentage of hydrogen after final result .	11.193 ± 0.0011
	100.057

It would now appear that the close agreement before shown was a mere coincidence, and that there must have been a small constant error either in our own process or in that of Dumas. Where the error lies further investigation can alone determine: for although, after a careful revision of our work, we can discover no flaw, no one can be confident that such a constant error as has already appeared may not hereafter be found—and certainty can only be secured after repeated confirmations by essentially different methods. While, therefore, we feel bound to acknowledge without delay the cause of constant error which Lord Rayleigh has pointed out, we give our corrected result as subject to further revision. It has been suggested by Lord Rayleigh, in a "Preliminary Notice" of his work on the relative densities of hydrogen and oxygen, of which advance sheets have been received while writing this note, that in our combustions the hydrogen may have been imperfectly burnt, especially as towards the last of the combustion it must have been greatly diluted (but with air). We have no decisive evidence on this point; but the whole course of our combustions assured us that this could not be the case. During the first stage of the combustion, when pure hydrogen was passing into the combustion tube, and while water was dropping into the condenser (Figure 4, page 96), there would often be several minutes—during which the larger part of the water was condensed—when no residual gas whatever would be seen to escape, and the bubbling of the gas through the sulphuric acid at the bend of the U tube made the least overflow perfectly evident. Again, the oxide of copper in the combustion tube was always reduced to a perfectly definite limit, leaving at least seven eighths of the tube in which the black oxide was apparently wholly unchanged. Further, it is not probable that an error arising from the imperfect combustion of the hydrogen would have a constant value. The unconsumed residue must vary greatly with the conditions of the experiment; and such an agreement as that exhibited by the results on page 107 could never have been obtained under such circumstances.

It seems unnecessary to add that every precaution was taken in our work which our experience could suggest, and that a great amount of labor was spent on such details which does not appear in the published results. Both the balances and weights employed were most carefully verified. The water formed by the combustion

was tested, and the dissolved air taken into account. We mention these points because they have been noticed by correspondents; but many similar details which were worked out and set one side we have not thought it necessary to describe in our paper. In writing such a paper elementary principles must be assumed.

In adopting Regnault's method for weighing the hydrogen used in our determinations, we assumed with him that the glass balloon used in the work remained practically constant, whether exhausted or filled with gas. We never questioned this assumption, not only because we had the greatest confidence in all Regnault's work, but also because we knew that he had himself carefully investigated the behavior of glass bulbs under pressure; and indeed he treats the subject fully in the paper immediately preceding his classical paper on gas density.[1] Moreover, we made with our apparatus a preliminary determination of the density of air, and obtained Regnault's number within the limits of the uncertainty in regard to the value of the force of gravity at this place. Regnault's values for the weight of one litre, not only of air, but also of nitrogen, oxygen, hydrogen, and carbonic dioxide, have been hitherto regarded as among the most trustworthy data of science. His determinations were all made by the method of counterpoise which we adopted in our work, and he used balloons of twice the volume of those we employed. When exhausted the glass must have been condensed to an even greater extent than has been shown above; but no account whatever is taken of this shrinkage. As Regnault's constants have been universally used, it is obvious that Lord Rayleigh's correction must be applied to all determinations of gas or vapor densities hitherto made, and to all atomic weight determinations of any kind which involve the calculation of the weight of a measured volume of any gas or vapor. Except, however, in the case of hydrogen, the correction will be inconsiderable.

J. P. C. CAMBRIDGE, *March* 15, 1888.

[1] Mémoires de l'Acad. Roy. des Sciences de l'Inst. de France, **21**, 106 and 121.

Contributions from the Chemical Laboratory of Wesleyan University.

VIII.—ON SOURCES OF ERROR IN DETERMINATIONS OF NITROGEN BY SODA-LIME, AND MEANS FOR AVOIDING THEM.

By W. O. Atwater.

The object of this paper, which concludes a series upon the same general subject, is to describe some further experiments in this laboratory, adduce results of observations elsewhere, and mention certain conclusions that seem warranted concerning sources of error in the determination of nitrogen in protein compounds, especially those of animal origin, by soda-lime, and the means by which they may be obviated.

Leaving out of account the apparent gain of nitrogen which may come from impure soda-lime, or from obvious errors in manipulation, to be mentioned beyond, the principal sources of error involve loss of nitrogen. Among the sources of loss are:

1. Incomplete ammonification of the nitrogen.
2. Dissociation or oxidation of the ammonia formed.
3. Failure of the ammonia to be completely caught and retained by the acid solution.

Loss by Incomplete Ammonification of Nitrogen.

Four ways suggest themselves by which nitrogen may fail to be changed into the form of ammonia and may hence be lost in soda-lime determinations, namely, by:

1. Incomplete decomposition of the nitrogenous substance, part of the nitrogen remaining in the partially decomposed (charred) residue.
2. Formation of compounds, *e. g.* cyanides, which remain in the tube.
3. Escape of nitrogen in the free state.
4. Formation of volatile nitrogenous products other than ammonia, which either pass through the acid solution unabsorbed, or if absorbed, are not detected by the subsequent titration with alkali or other means used to find the amount of nitrogen in the solution.

As no especial study of the first three of these sources of loss has been made here, I need only refer to them briefly.

To insure complete decomposition, fine pulverisation, thorough mixing with soda-lime, and heating, at sufficiently high temperature, until no charred residue remains, would seem to be the requisites. As to the fineness of pulverisation needed there seem to be differences of opinion among chemists. Ritthausen[1] and Gruber,[2] for instance, lay great stress upon it. Gruber cites comparative determinations of nitrogen in flesh in which the incorrect results fell nearly 0.9 per cent. below the correct ones, and the only difference in the conduct of the analyses was that, in the defective ones, the "Fleischpulver noch einzelne wahrnehmbare Körnchen enthielt." Johnson and Jenkins, on the other hand, say that: "Contrary to what is commonly stated, fine pulverisation of the substance to be analysed is not necessary. If the substance will pass holes of one millimeter in diameter it is fine enough. A sample of dried blood which passed through a sieve with meshes one millimeter in diameter gave 7.58 per cent. of nitrogen. A portion of the same, ground extremely fine with sand, gave 7.64 per cent. Fish-scrap passed through the same sieve gave 8.98 per cent of nitrogen; when ground with sand, 8.95 per cent. A second sample of fish, sifted as above, gave 8.69 per cent. of nitrogen. By the absolute method it yielded 8.79 per cent."[3]

The not inconsiderable experience of this laboratory confirms very decidedly the opinion last quoted. We have for a number of years used a sieve with circular apertures of one millimeter diameter. A large number of comparisons of results obtained by the soda-lime and absolute methods, and in a considerable number of cases with that of Kjeldahl, have given results so concordant as to persuade us that particles which have passed through this sieve are fine enough.

In absence of definite statements as to the actual fineness which is regarded as desirable by those who insist upon very fine pulverisation, I am inclined to suspect that the standard adopted by Johnson and Jenkins, and in this laboratory, would perhaps be regarded as satisfactory in respect to fineness by them and by investigators generally. Certain it is that when, as in a number of instances, we have tried to use a sieve of one half millimeter aperture, we have found the process of grinding painfully laborious and time-consuming, even with the use of a mill especially devised

[1] Jour. prakt. Chem. **116**, 1874, p. 17. [2] Ztschr. f. Biol. **16**, 380.
[3] Report of Conn. Agl. Expt. Station, 1878, 116.

for the purpose and exceeding in convenience all other forms which I have seen.

As to formation of cyanogen or other compounds which would be retained by combining with the bases of the soda-lime, I have been unable to find any experimental facts which would lead to the supposition that there is any considerable danger of loss in this way in the combustion of ordinary animal and vegetable substances, provided the soda-lime contains enough water, and the quantities of soda-lime and substance, temperature, and other conditions are appropriate.

Regarding the escape of free nitrogen by decomposition of such nitrogenous compounds as those in question (leaving out of account the dissociation or oxidation of ammonia formed from them), I am likewise unable to find any facts which imply special danger of loss in this way, although it might, perhaps, be feared from such observations as that of Liebermann that albumin on being heated with caustic baryta to 150° yields free nitrogen.[1] The main assurance that it does not escape to any great extent when the operation is rightly conducted, is found in the agreement of the results obtained with those obtained by other methods.

The presence of nitrates, as impurities in soda-lime or otherwise, may cause loss of nitrogen, perhaps as free nitrogen, but this is of course simply a contingency to be feared from careless work.

Loss of Nitrogen by Formation of Volatile Products other than Ammonia.

As long ago as 1860 Mulder called attention to the danger of loss by formation of volatile products which, escaping ammonification within the tube, were either not caught by the acid or, if retained, escaped determination by either titration with alkali or precipitation by platinic chloride.[2] About the same time Strecker observed that guanidine salts failed to yield all their nitrogen as ammonia with soda-lime.[3]

Ritthausen and Kreussler were unable to get more than 7.9 per cent. of nitrogen from leucine by soda-lime alone, even when the greatest care was taken to pulverise and mix it with the soda-lime, and 120 times as much soda-lime as substance was used. Adding sugar, however, they got as high as 10.43 per cent., very nearly the

[1] Jbt. Ag. Chem. **21**, 766. See also Wanklyn and Gamgee, J. Chem. Soc. **21**, 1868, 25.
[2] Chem. Centrbl. 1861, 44. [3] Ann. Chem. (Liebig) **118**, 1861, 161.

theoretical amount, and Ritthausen suggests that the trouble with leucine, as with other compounds, may be that volatile cleavage products are formed and pass over the soda-lime without their nitrogen being changed to ammonia.[1]

Märcker insists that aniline-like products may be given off instead of ammonia, and finds proof of this in observations that some substances, as for instance gluten and leucine, gave nearly or quite their full amount of nitrogen with platinic chloride, while there was decided loss by titration with alkali. With blood albumen and horse-flesh, however, there was a loss by titration which the platinic chloride did not amend, and which can be explained by assuming that products were formed which are not precipitated by the platinic chloride, which does precipitate aniline and kindred compounds.[2]

Among the materials in which Nowack and Seegen failed to obtain the normal quantity of nitrogen (see beyond) by soda-lime was barium kynurenate. Gruber very aptly remarks that as kynurenic acid has been shown to be a derivative of quinoline, the failure may have been due to distillation of the latter.[3]

E. Salkowski suggests that in determinations of albuminoids by soda-lime, bases of the pyridine series may be formed and escape ammonification. He also suggests that a substance with red color which he obtained in burning at low heat with a small quantity of soda-lime may perhaps be the chromogen of urobilin.[4]

Kjeldahl in the discussion of his method for nitrogen determinations, referring to Mulder's advice to avoid any large amount of vacant space inside the combustion tube, states a very interesting observation of his own. In making combustions of quinine-hydrochloride with soda-lime, he found that when the soda-lime was loosely packed and shaken so as to leave a channel in the ordinary way, he obtained only about one half the nitrogen, while with the conditions in every respect the same except that the tube was well packed with soda-lime so as to leave a minimum of vacant space, he obtained practically the whole of the nitrogen as ammonia by titration. He attributes the loss in the first instance to the formation of volatile nitrogenous products which, not being brought into intimate contact with the soda-lime, escaped ammonification.[5]

[1] J. prakt. Chem. **111**, 1871, 310.
[2] Archiv Physiol. (Pflüger) **8**, 1874, 207.
[3] Ztschr. f. Biol. **16**, 1880, 377.
[4] Ztschr. anal. Chem. **16**, 261 and 408.
[5] Ztschr. anal. Chem. **22**, 1883, 380. See also Arnold, Ber. d. chem. Ges. **18**, 1885, 809.

The experiments cited by Mr. Ball and myself[1] in the previous article of this series bear striking testimony to the danger of loss if there is not sufficient contact between the gaseous distillation products and the heated soda-lime. In determinations of casein by our usual method (which involves close packing of the soda-lime in the tube, the use of coarse particles of soda-lime for the anterior layer, heating the anterior layer before the distillation products begin to be developed, and keeping it well heated until the combustion is finished), the whole of the nitrogen, 12.43 per cent., was obtained as ammonia. But when a channel was left in the tube (and fine soda-lime was used for the anterior layer) so that there was less contact between distillation products and heated soda-lime, the nitrogen obtained as ammonia amounted to only from 12.25 to 11.65 per cent. of the weight of the casein instead of 12.43 per cent.; that is to say, from 1.4 to 6.4 per cent. (on the average 3.3 per cent.) of the whole nitrogen escaped ammonification. When, again with the channel, the anterior layer was made shorter, 7.5 cm. instead of 12 cm., the nitrogen obtained as ammonia fell as low as 10.51 per cent., the rest, 15.4 per cent. of the whole, escaping ammonification. The average loss under these last conditions was 6.4 per cent. of the whole nitrogen. Even more striking illustrations of the failure of distillation products to be changed to ammonia are given in the experiments with strychnine described in the same article. In these but a fraction, at times very small, of the total nitrogen was obtained as ammonia, although especial effort was made to secure complete ammonification.

But little consideration of the matter is needed to show that the formation of volatile nitrogenous products which would escape ammonification by the soda-lime and detection in the acid is a very natural occurrence.

The protein compounds when subjected to destructive distillation yield a great variety of products, among which are, besides water, carbon dioxide, hydrogen sulphide, and hydrocarbons, a great variety of volatile nitrogenous compounds, including ammonia, ammonia salts of the fatty acids, amines derived from the paraffins, members of the aniline and pyridine series, pyrrol, etc., etc.[2] By heating in the presence of alkalies and other reagents a great variety of other compounds, with the rest a number of acids of the

[1] This Journal **10**, 113.

[2] See Handw. d. Chem. **2**, 1161–1173, and E. Salkowski, Ztschr. anal. Chem. **16**, 1877, 261 and 408.

fatty acid series and amido acids belonging to this and the aromatic series, among which latter are leucine and tyrosine. By the action of enzymes and microbes, products akin to the alkaloids are formed. The alkaloids break up into compounds such as were mentioned above, and numerous others including members of the quinoline series.

Now these nitrogenous products vary greatly in respect to their volatility and the ease with which they are changed to ammonia when heated in presence of soda-lime (*i. e.* of water vapor at high temperature). The specific data at hand regarding the ease with which they are ammonified are meagre. There are, however, observations bearing upon this point. For instance, Goldberg finds that some of the more complex azo-compounds, with soda-lime, yield all their nitrogen as ammonia, while the simpler ones fail to do so, part escaping.[1] There is nothing more natural than that in soda-lime combustions such volatile nitrogenous products should be formed and escape ammonification.

A fact of interest here is that some, at least, of the compounds which are most difficult to determine by soda-lime are the ones that are most readily broken up into very volatile products. Such are guanidine, kynurenic acid which may yield quinoline, leucine, and quinine and other alkaloids. It is also worth noting that some of the alkaloids, the nitrogen of which it is so difficult to transform entirely into ammonia by soda-lime, manifest a similar behavior in treatment with sulphuric acid and other reagents by Kjeldahl's method,[2] and perhaps for similar reasons.

In looking over the literature of the subject, which is quite extensive, one cannot help being impressed by the fact that certain nitrogenous compounds very frequently, and others almost uniformly, fail to yield all of their nitrogen in the form of ammonia when heated with soda-lime. Whatever may be the differences of manipulation of different experimenters, nearly all find it impossible to get all of their nitrogen in that form from such substances as leucine and some of the alkaloids. But in some cases, as for instance those of Märcker and Abesser above quoted, the nitrogen has been obtained by precipitating platinic chloride even when it was not obtained by titration. Leucine[3] is in this respect an especi-

[1] Ber. d. chem. Ges. **25**, 46.

[2] Ztschr. anal. Chem. **22**, 1883, 379.

[3] *E. g.* Märcker and Abesser, loc. cit.; Ritthausen and Kreussler, J. prakt. Chem. **111**, 1871; Ritthausen, ibid. **116**, 1874, 17.

ally refractory compound, though chitin,[1] gluten-protein,[2] and, in some instances, casein[3] (milk) and peptones,[4] have given trouble in this way.

The interesting researches of Schützenberger[5] have indicated that the protein compounds (albuminoids and gelatinoids) are made up of a variety of simpler compounds, among which leucine and another, or perhaps several other compounds closely allied to it, are among the important constituents. That is to say, under the influence of various agencies the protein compounds split up into a large variety of simpler compounds, among which leucine and its congeners play an important part. That these latter might be easily formed from protein compounds in the breaking up which occurs in the ordinary heating with soda-lime is a very natural inference from the facts at hand. But from its constitution, leucine might be expected to readily be split up into volatile nitrogenous compounds. Such observations as those of Märcker and Strecker, above quoted, would seem to give reasonable assurance that it actually does so. In view of these facts it will be easy to assume that in ordinary combustions by soda-lime there is a tendency to the formation of nitrogenous distillation products such as come from leucine and analogous compounds, and which would escape ammonification.[6] Such being the case, it is easy to see how volatile nitrogenous compounds might often escape ammonification unless the greatest pains were taken to insure the most perfect contact between them and the heated soda-lime (heated water vapor), and that sometimes the ammonification might be incomplete despite the greatest care. If this be correct, the difficulty of getting all of the nitrogen of peptones into form of ammonia would accord with the fact that the peptones are products of change of the albuminoids, which change, carried further, results in the cleavage of the latter into leucine and other allied products. It would also be easy to theorise regarding the constitution of the alkali albumins and casein, and to imagine that they might like-

[1] Bütschli, Ztschr. anal. Chem. **16**, 1877, 409.

[2] Märcker and Abesser, loc. cit.; Kreussler, Landw. Vs. St. **31**, 1884, 248. See also Ritthausen, loc. cit.

[3] Lehmann, Ztschr. anal. Chem. **15**, 1876, 113; Musso, ibid. **16**, 1877, 413; Menozzi, Jsb. Agr. Chem. **21**, 1878, 474; Kreussler, loc. cit.

[4] Gruber and Feder, Ztschr. f. Biol. **16**, 1880, 381.

[5] Bull. Soc. Chim. **23-30**, 1875-1878, and Chimie Générale **131**, 407.

[6] See also Hofmann, Ann. Chem. (Liebig) **79**, 29; Wertheim, Jour. prakt. Chem. **53**, 431; Williams, loc. cit. **76**, 383; and Michael, this Journal **7**, 182, for decompositions of alkaloids and other compounds, bearing upon this question.

wise be on the way toward the process of cleavage by which leucine and its decomposition products are produced. Of course this is speculation, but it at least helps us to see how the observed facts might occur; and irrespective of any such hypotheses, the known facts are sufficient to warrant the assumption that under the influence of high heat in the presence of soda-lime, numerous volatile nitrogenous compounds might be expected to be formed, some of which would resist ammonification; and that certain classes of protein compounds would be especially prone to such decomposition, even though, in the present state of our knowledge, we are unable to say just exactly what those compounds are, or what are the processes of cleavage they go through, or what are the nitrogenous products that resist ammonification. An illustration of the difficulty of ammonifying some of these volatile compounds is found in the above mentioned case of strychnine in the experiments detailed in the previous article of this series. Neither the most painstaking effort to secure contact between the gases and the soda-lime by the Will-Varrentrapp method, nor by the greatest care in heating by that of Kjeldahl, sufficed to convert all the nitrogen into ammonia. On the other hand, the results with casein, when means were taken to secure adequate contact with soda-lime and to avoid dissociation, were most satisfactory. But when a channel was left in the tube so that the distillation products were not brought into close contact with the soda-lime, the loss was at times very large.

The lesson which all these considerations teach, and which is enforced by those cited in the previous articles, is the importance of providing intimate and sufficient contact between the distillation products and the heated soda-lime. This is done by fine pulverisation and intimate mixture of substance with soda-lime; by having the tube closely packed with soda-lime to avoid open spaces; by providing a long enough anterior layer of soda-lime, and by heating this layer well before the gases are disengaged, and keeping it well heated until the combustion is finished. At least such seems to me the just inference from the facts at hand.

Loss of Nitrogen in Distillation Products as indicated by Coloration of Acid Solution in the Nitrogen Bulb.

It is frequently urged, *e. g.* by Johnson and Jenkins,[1] that the combustions should be so conducted as to avoid any considerable

[1] Report of Conn. Ag'l Exp't Station, 1878, 116.

discoloration of the acid solution, since the coloring matter may contain nitrogen. I have been at no little pains to learn how to insure this result. In how far it may be accomplished by the use of slaked lime, as suggested by Johnson,[1] I am unable to say, having had no experience. One of my assistants, Mr. G. P. Merrill, made, at my suggestion, a considerable number of combustions with nitrogen-free stearin at different temperatures, with varying degrees of rapidity and different lengths of anterior layers of anterior soda-lime. In general we found that the more the gaseous products of distillation in the tube were brought into contact with the soda-lime, the less was the discoloration manifested. But we were unable, even with the highest heat, very long tubes, and slow conduct of the operation, to secure a complete combustion of the distillation products; materials with the odor of hydrocarbons being always given off in considerable quantities. These and other similar experiences gave me the impression that the largest conveniently practicable contact between the gaseous products of distillation and the soda-lime was desirable, and on that account we practiced for a considerable time the use of long tubes with a long layer of soda-lime. Several circumstances, however, have shaken our faith in the need of this precaution. One is found in the comparative results of determinations with the long and the short tubes detailed in Article IV of this series,[2] in which the same quantities of nitrogen were obtained with tubes of 40 cm. and closely packed anterior layers of soda-lime of 12–15 cm., as with tubes of 60–75 cm. and correspondingly longer anterior layers. The comparative results in the combustion of ammonium sulphate in the long and short tubes, cited in the same article, seem to preclude the assumption that any loss of nitrogen from dissociation in the long tubes could have compensated for what would otherwise have been a gain from more complete ammonification. This effort to secure more perfect ammonification by means which tend to prevent the formation of colored compounds was therefore without avail. Another fact which militates against the idea that coloration of the solution necessarily indicates the presence of nitrogen compounds which have escaped ammonification, is found in the results of quite extensive experience in this laboratory, in which we have taken pains to note through a period of several months the amount of discoloration in the acid solution as measured by the eye. When we came to collate these

[1] This Journal **6**, 60.

[2] Ibid. **9**, 320.

observations, which include many scores of determinations, we found to our surprise that we had, with no exceptions exceeding the practically unavoidable variation of duplicate analyses, as much nitrogen with the considerably discolored and turbid as with the nearly clear and colorless solutions; nor did the quantity of nitrogen average materially less in the former than the latter.

Johnson[1] mentions that in combustions with the soda-lime made from slaked lime and sodium carbonate, as suggested by himself,[2] "the acid in the bulk-tube is frequently colored more or less deeply red." On one occasion, in making some combustions with Johnson's soda-lime, we noticed that the acid in the bulb became reddish in color during the combustion. The soda-lime was a little moist. It was dried and the same combustions repeated. The solution then remained perfectly colorless. On another occasion I noticed a similar red color in the solution when moist ordinary soda-lime was used. The same soda-lime was dried and the combustions repeated. The solutions were then colorless. In each of these two cases the solution was very clear with both the moist and the dry soda-lime, and the red color with the moist soda-lime was very pronounced. What the coloring matter was I am unable to state, but the observation seems to be very similar to the one by E. Salkowski, above cited, from which he infers the presence of the chromogen of urobilin.

The following series of determinations of nitrogen in a specimen of (probably impure) albumen prepared from beef, include the observations just referred to as made with Johnson's soda-lime, and may be worth citing.

The combustions were conducted at what we have called "high heat,"[3] to wit, the highest heat the tubes of the most difficultly fusible Bohemian glass we could obtain would bear without bursting. The time of the combustions was about 60 minutes in each case. The percentages of nitrogen are calculated on water-free substance. The determinations were made by a student in this laboratory some years ago when the investigations here reported were being entered upon. The results are given in Table I.

The differences in results, which vary from 15.71 to 16.24 per cent., I presume to be due to differences in the charging of the tube. That is to say, it seems to me most probable that the low results in

[1] Loc. cit. 61. [2] This Journal **1**, 77.
[3] See Article IV of this series, this Journal **9**, 315.

Nos. 3-8 were due to loose packing of the soda-lime in the tube, and consequent incomplete contact of distillation products with the soda-lime. I can think of no other explanation of the wide discrepancies. There is perhaps a relation beween either the clearness or the color of the solution and the apparent accuracy of the results, though it is not very pronounced.

TABLE I.

Determinations of Nitrogen in Albumin.

Number	1	2	3	4	5	6	7	8
Soda-lime	Ordinary.		Johnson's.				Ordinary.	
Length of tube . .	75 cm.	75 cm.	75 cm.	75 cm.	40 cm.	40 cm.	40 cm.	40 cm.
Solution	Nearly clear. Colorless.		Perfectly clear. Deep red.		Somewhat turbid. Colorless.			
Per cent. N found	16.24	16.25	16.05[1]	16.07[1]	16.00	15.78	15.71	16.10

[1] Soda-lime moist.

Thus in Nos. 1 and 2 the determinations were apparently correct (though there is no proof that such was the case). The solution was colorless and had but little matter in suspension. In Nos. 3 and 4, in which the soda-lime was moist, there was no visible suspended material, but the solution was red, and less nitrogen by about 0.2 per cent. was obtained. In Nos. 5 and 6, which were duplicates of Nos. 3 and 4, except that the soda-lime was dried, the solution was colorless but somewhat turbid from suspended matters, and still less nitrogen was obtained. In Nos. 7 and 8, which were duplicates of Nos. 1 and 2, except that the tubes of the latter were of extra length, the solution was somewhat turbid and the percentages of nitrogen were small.

When these results were obtained we were inclined to interpret them as confirming the idea that turbidity and color in the solution implied loss of nitrogen. But perhaps all that they amount to is to furnish illustrations of the general facts that neither agreement of duplicates (compare 1 and 2 with 3 and 4) nor the clearness or turbidity, nor the presence or absence of color of the solutions, can be taken as a test of the correctness or incorrectness of the determinations.

Although we were somewhat surprised to find, in comparing the large number of results referred to above, that the nitrogen obtained where the solutions were nearly clear and colorless averaged just about the same as where they were more turbid or colored, yet it is after all not so strange, in view of the facts that:

(1). Non-nitrogenous materials, such as the decomposition products of fats and carbohydrates, and probably the non-nitrogenous cleavage products of protein compounds as well, may impart turbidity and color to the solution. That is to say, neither color nor turbidity is at all an evidence of presence of nitrogenous matters.

(2). Even if the color be due to nitrogen compounds, it does not by any means prove the presence of enough to have any material effect upon the result, since the quantity which would color a small amount of solution might easily be far too slight to be revealed by titration.

(3). Many volatile nitrogenous compounds such as we should expect to escape ammonification in soda-lime combustions, *e. g.* amido acids and amines, are colorless and soluble. Hence absence of turbidity or color is no proof of absence of non-ammonified nitrogen compounds.

I do not by any means mean that turbidity and color are not to be avoided if practicable, or that they do not indicate imperfect combustion. What I wish to urge is, that neither color nor turbidity, unless excessive, is an indication of a bad, or their absence a proof of a good determination.

The danger of loss of nitrogen through oxidation by nitrates occurring in the soda-lime as impurities, or introduced with the substance to be analysed, requires no discussion here.

What has been urged regarding incomplete ammonification of nitrogen of protein compounds may be briefly recapitulated as follows:

(1). Loss by incomplete decomposition would seem to be best prevented by fine pulverisation of substance, thorough mixing with plenty of soda-lime, and heating until no considerable amount of charred residue is left.

(2). Loss by formation of cyanides which combine with the bases of the soda-lime, does not seem to occur if the substance is mixed with enough soda-lime of proper water content and properly heated. Comparison of results of properly conducted combus-

tions with those obtained by other methods implies no considerable escape of nitrogen in the free state.

(3). There is great danger of loss of nitrogen in volatile distillation products which escape ammonification. With some compounds, as alkaloids and leucine, this seems extremely difficult to avoid; but with the ordinary protein compounds of animal and vegetable tissues, and with the casein of milk, the experience of this laboratory implies that complete ammonification can be insured by providing for sufficient contact of the substance and its decomposition products with heated soda-lime, (*i. e.* with water vapor at high temperature).

(4). This needed contact is best secured by (*a*) thorough mixing of substance with soda-lime; (*b*) use of soda-lime which contains a rather large proportion of lime, is not too fusible and does not shrink too much in heating; (*c*) carefully avoiding a channel; (*d*) providing a considerable anterior layer of soda-lime; (*e*) heating this latter to dull redness before bringing the heat to bear upon the substance, and keeping it hot until the combustion is done.

(5). While it is desirable to avoid the escape of matters which color the acid solution in the nitrogen bulb and render it turbid, the presence of these is not an indication of incomplete, nor their absence an indication of complete ammonification of the nitrogen.

(*To be continued.*)

Contributions from the Chemical Laboratory of the University of Cincinnati.

XXXVII.—ON THE ACTION OF SILICON TETRAFLUORIDE ON ACETONE.

By T. H. Norton and J. H. Westenhoff.

Among the few typical inorganic compounds whose reactions with organic substances have either been entirely neglected or but slightly studied, silicon tetrafluoride is probably the most important.[1]

[1] After the completion of most of the work described in the present paper, Prof. C. L. Jackson and A. Comey published a note in the Berichte der deutschen chemischen Gesellschaft (**19**, 3194), in which they describe the action of silicon fluoride on aniline, giving rise to the compound $(C_6H_5NH_2)_3(SiF_4)_2$. Prof. Jackson has courteously informed us that their investigation would be, at least for the present, confined to the study of the reactions of the fluoride with amines, and that the examination of the reactions with oxygen compounds lay open to us.

With the intention of examining the action of the fluoride on several classes of compounds, we have studied first its reaction with acetone. This was chosen on account of the readiness with which acetone enters into reaction with almost all of the reagents employed in organic chemistry.[1]

The silicon fluoride used in the reaction was generated by gently heating on a sand-bath, in an ordinary bottle of thick glass, a mixture of finely powdered fluorspar, finely powdered glass, and sulphuric acid. The current of gas was passed slowly into 825 grams of acetone (boiling point 56°-58°) kept at 0°. The liquid, shortly after the entrance of the gas, assumed a dark color, which increased in intensity as the operation continued. When the absorption seemed complete the evolution of gas was stopped, and it was found that the 825 grams of acetone had absorbed 375 grams of silicon fluoride, or 45.3 per cent. of its weight. The dark colored product thus obtained gave off vapors of SiF_4 freely when exposed to the air. A very slight amount of silicic acid was deposited during the process of absorption.

The liquid was first heated in a flask provided with an inverted condenser for the purpose of removing the excess of fluoride absorbed. In a short time it underwent a loss in weight of 100 grams. There remained 1100 grams of the liquid, and this was next subjected to distillation. The distillate weighed 600 grams, and 435 grams of a tarry residue remained in the retort. The clear liquid obtained by this means was next subjected to a series of seven fractional distillations. Tarry residues remained in the distilling flask after each series of distillations, 25 grams after the first series and an average of 9 grams after each of the other series. During each of the seven series of distillations there was likewise an average loss of 22 grams, due apparently to the liberation of SiF_4.

The seventh fractionation gave the following results:

Fraction boiling at 56°-60°	199 grams.
60°-65°	58
65°-70°	27
70°-80°	19
80°-90°	14
90°-100°, A	73
90°-100°, B	50

[1] Compare more especially Landolph, Ber. d. chem. Ges. **12**, 1579, action of boron trifluoride on acetone.

Of these fractions the one distilling at 56°–60° was naturally nearly pure acetone. The smaller fractions between 60° and 90° were colorless when distilled, but in an hour or two assumed a dark brown hue, indicating the presence of unstable compounds, and consequently of rapid decomposition. Two fractions boiling between 90° and 100° were obtained—A, a liquid lighter than water, and B a liquid heavier than water. These fractions were non-miscible.

The following are the specific gravities of the different fractions:

56°–60°	0.818	80°–90°	0.942
60°–65°	0.851	90°–100°, A	0.904
65°–70°	0.873	90°–100°, B	1.36
70°–80°	0.898		

The fraction A was slightly unstable, the colorless liquid darkening gradually on standing, although in a much less marked degree than was the case with the fractions obtained at lower temperatures. Silicic acid also separated out in the form of a gelatinous mass when the liquid was allowed to stand for some time. It seemed to contain no fluorine, for, on heating with sulphuric acid and passing the vapors through water, no separation of silicic acid took place, as is the case when vapors of silicon fluoride come in contact with water.

The fraction B was of a light yellow color, and was the only product of the distillation not subject to a more or less rapid change in coloration.

These two products were the only ones subjected to analysis. The lower fractions were not only of comparatively slight amount, but also too unstable to offer any hope of satisfactory analytical results.

Analysis of the fraction A.—The combustions were made with lead chromate.

I. 0.1089 gram of substance gave 0.1072 gram of H_2O, equal to 0.0119 gram of H or 10.92 per cent.; and 0.2538 gram of CO_2, equal to 0.0690 gram of C, or 62.71 per cent.

II. 0.2927 gram of substance gave 0.3024 gram of H_2O, equal to 0.0336 gram of H, or 11.7 per cent.; and 0.6687 gram of CO_2, equal to 0.1824 gram of C, or 62.3 per cent.

The silicon was determined by treating the liquid with a concentrated solution of caustic potash, acidifying with hydrochloric

acid, and following out the ordinary method for the determination of silica.

I. 1.1984 grams of substance gave 0.061 gram of SiO_2, equal to 0.028 gram of Si, or 1.44 per cent.

II. 1.12 grams of substance gave 0.0383 gram of SiO_2, equal to 0.0178 gram of Si, or 1.33 per cent.

Polis[1] gives a method of determining silicon in organic compounds which consists essentially in dissolving the substance in warm sulphuric acid and then adding a concentrated solution of potassium permanganate to complete oxidation. This method was also used with the following result:

III. 0.7718 gram of substance gave 0.0465 gram of SiO_2, equal to 0.0217 gram of Si, or 2.63 per cent.

	Found.		
	I.	II.	III.
H	10.92	11.7	...
C	62.71	62.3	...
Si	1.44	1.33	2.63

Analysis of the fraction B:

I. 0.2532 gram of substance burnt with lead chromate gave 0.2309 gram of H_2O, equal to 0.0256 gram of H, or 10.11 per cent.; and 0.0927 gram of CO_2, equal to 0.0255 gram of C, or 10.07 per cent.

II. 3.318 grams of substance gave on treatment with caustic potash 0.3979 gram of SiO_2, equal to 0.1855 gram of Si, or 5.55 per cent.

III. 2.7146 grams of substance gave by the same method 0.3138 gram of SiO_2, equal to 0.1463 gram of Si, or 5.39 per cent.

IV. 0.7168 gram gave on treatment with permanganate 0.011 gram of SiO_2, or 0.0051 gram of Si, equal to 0.714 per cent. (This method of Polis was evidently not adapted to the analysis of this substance, as silicon fluoride was evolved in notable quantity on the addition of the sulphuric acid.)

	Found.	
	I.	II.
H	10.11	...
C	10.07	...
Si	5.55	5.39

It was observed in the above mentioned combustion that a slight deposition of silicic acid took place in the calcium chloride tube

[1] Ber. d. chem. Ges. **19**, 1024.

used for the absorption of water, resulting undoubtedly from the liberation of silicon fluoride during the operation and its decomposition by the moisture gathered in the tube. The percentages for hydrogen are therefore higher than the truth. An element of uncertainty also exists with regard to the silica determinations, especially in the presence of fluorine.

The analytical data are exceedingly unsatisfactory, giving but little clue to the probable composition of the two products.

In fraction A the analyses would indicate the presence of about 25 per cent. of oxygen, as there seemed to be no fluorine in this product. The percentage of carbon in this liquid corresponds very closely to the percentage of carbon in acetone, and it apparently is a compound of acetone with a very small amount of silicon or silica.

In fraction B the small amount of carbon, the larger amount of silicon, and the fact that about 75 per cent. of the liquid consists of oxygen and fluorine in unknown proportions, render it impossible to make any supposition with regard to the probable composition of the substance which seems to be the most stable and the most important product of the reaction.

The total absence of a method for determining fluorine in organic substances brings such an element of uncertainty into the examination of a compound containing both fluorine and oxygen that we have continued the investigation no further in the direction indicated, feeling that much more satisfactory work can be accomplished by confining ourselves to the study of the reactions of silicon fluoride with non-oxygenated bodies.

XXXVIII.—ON THE LIMITS OF THE BROMINATION OF ACETONE AT 0°, AND ON THE ACTION OF AMMONIUM SULPHOCYANIDE ON MONOBROMACETONE.

By T. H. Norton and J. H. Westenhoff.

The direct action of bromine on acetone has been studied by Linnemann,[1] Emmerling and Wagner,[2] and Mulder.[3] The first states that on mixing the two at 0° he obtained an addition product, $C_3H_4O.Br_2$, in company with epibromhydrine, and acroleïn

[1] Ann. Chem. **125**, 307. [2] Ibid. **204**, 89. [3] J. prakt. Chem. **91**, 475.

compounds. Emmerling and Wagner prepared monobromacetone by passing a current of air saturated with bromine vapors through ice-cold acetone. Mulder obtained a tetrabromacetone and a pentabromacetone by adding a large amount of bromine to acetone kept at or below 0°. As neither Linnemann nor Mulder gives analytical data, and Linnemann gives also no description of the physical properties of his additive product, it seemed of interest to us to determine the limits within which bromine can be directly substituted for hydrogen in the acetone molecule at a low temperature. At the same time we wished to see whether it would be possible to prepare directly the unsymmetrical dibromacetone which Sokolowsky[1] obtained by allowing two molecules of bromine to act on acetone in very dilute aqueous solution.

For this purpose 100 grams of acetone were placed in a flask surrounded by crushed ice, and 235 grams of bromine were slowly added. The product was then thoroughly washed with water to remove the hydrobromic acid formed, and dried over calcium chloride. It weighed 248 grams, was of a reddish brown color, and possessed a specific gravity of 2.1. (The specific gravity of monobromacetone is 1.99, and that of unsymmetrical dibromacetone 2.5.)

This product was treated again with bromine, 100 grams being added under the observance of the same precautions. After washing and drying the liquid resulting from the second treatment, we found that there was no noticeable change in the color, but that the specific gravity had risen to 2.35. The same process was repeated and 100 grams of bromine were again introduced. After this third addition a notable amount of free bromine was present in the liquid, which had not hitherto been the case. During the washing of this product in order to remove the free bromine and hydrobromic acid, the volume was at first but little changed. After a short time it diminished rapidly with each subsequent washing. The final product had a deep red color, and possessed a specific gravity of but 2.2. The odor of free bromine was quite noticeable after it had been allowed to stand for a short time.

Judging from these results it would seem to be impossible to convert acetone entirely into a product containing more than one atom of bromine by the direct addition of bromine at a low temperature,

[1] Jour. of the Russian Chem. Soc. 8, 330.

although the specific gravities would indicate that we obtained a mixture of monobromacetone and dibromacetone containing over 50 per cent. of the latter compound. There appears to be a certain limit to the action of the bromine beyond which rapid decomposition sets in, as seen above. In the case of chlorine, on the contrary, it is possible to substitute from one to five atoms of hydrogen in acetone by the direct action of the halogen.

We could obtain no trace of the additive product mentioned by Linnemann. His description of this substance is exceedingly meagre. He states that it results from the addition of ice-cold bromine to cold acetone, that it is exceedingly unstable, decomposing at ordinary temperatures with separation of hydrobromic acid and giving off the odor of acrolein. The same decomposition occurs on distillation, vapors of hydrobromic acid being driven off and the distillate showing every property of acrolein.

We find, on the contrary, while carrying out the experiment under the same conditions, that the reaction is not additive, but purely one of substitution. The bromine replaces hydrogen, hydrobromic acid is formed, and the crude product is simply the mixture of the two substances, a brominated aceton and hydrobromic acid, from which the latter constituent is removed at once by washing. As it is well known that monobromacetone as obtained by other methods is quite susceptible of decomposition, especially when not pure, *i. e.* not freed from the acid formed during the reaction, and also that on distillation it yields products similar to those described by Linnemann, we surmise that the substance supposed by the latter to be $C_3H_6O.Br_2$ was simply the mixture of the two products of the reaction $C_3H_6O + Br_2 = C_3H_5BrO + HBr$, not yet freed from the acid by washing. The absence of analytical data and any description of physical properties in Linnemann's account prevents us from offering more than a surmise.

Action of Ammonium Sulphocyanide on Monobromacetone.— Monochloracetone and ammonium sulphocyanide act upon each other with ease in an alcoholic solution, the product of the reaction being the sulphocyanide of sulphocyanpropimine:[1]

$$C_3H_5ClO + 2NH_4SCN = \begin{array}{l} CH_2SCN \\ | \\ CNH.HSCN \\ | \\ CH_3 \end{array} + NH_4Cl + H_2O.$$

[1] Tcherniac and Norton, Ber. d. chem. Ges. **16**, 345.

As the corresponding bromine derivative of acetone is more easily prepared than its chlorine homologue, it seemed of interest to us to ascertain whether it was capable of replacing monochloracetone in the above mentioned reaction.

The monobromacetone used was prepared according to the method indicated by Emmerling and Wagner,[1] which consists in conducting a current of air laden with bromine vapors through ice-cold acetone. 100 grams of acetone and 138 grams of bromine gave 110 grams of monobromacetone after thorough washing and drying over calcium chloride. This product had a specific gravity of 1.99, and the analysis gave 58.10 per cent. of bromine (the theory requires 58.45).

The method used in the preparation of sulphocyanpropimine from monochloracetone was followed in the treatment of the bromine compound. 15.5 grams of ammonium sulphocyanide were dissolved in 93 grams of 90 per cent. alcohol. The equivalent amount of monobromacetone—14 grams—was then added, and the mixture was kept at a gentle heat for over a day, during which time ammonium bromide continued to separate out.

The alcoholic solution, which had assumed a deep red tint, was then filtered from the residual ammonium bromide and evaporated to dryness on the water-bath. The dark residue obtained by this means was treated with four times its weight of water and allowed to stand for three days. The resultant yellow solution was separated from a black tarry residue and carefully examined. It was found to contain some ammonium bromide and ammonium sulphocyanide with a small amount of coloring matter, but no trace of sulphocyanpropimine sulphocyanide could be detected. The operation was repeated several times, but in all cases with equally fruitless results.

It seems probable, therefore, that while a certain amount of sulphocyanacetone, $CH_3CO.CH_2SCN$, may be formed, as is evident from the amount of ammonium bromide produced, the monobromacetone is not susceptible of change into the corresponding imine.

[1] Ann. Chem. **204**, 28.

XXXIX.—ON THE ACTION OF CHLORINE ON ACENAPHTHENE.

By J. T. Kebler and T. H. Norton.

The only halogen derivatives of acenaphthene thus far known are bromacenapththene, $C_{12}H_9Br$, dibromacenaphthene, $C_{12}H_8Br_2$, and dibromacenaphthene bromide, $C_{12}H_8Br_2.Br_4$; all of which are obtained in well defined crystalline forms. We have submitted this hydrocarbon to the action of chlorine in the hope of increasing the small number of acenaphthene derivatives. The operation was conducted in the following manner: Acenaphthene (melting point 95°) was introduced, in portions of 50 grams, into a U tube connected with a chlorine generator. A current of chlorine, well washed and perfectly dry, was passed through the hydrocarbon until no further increase of weight could be obtained. The acenaphthene was attacked at once, even at ordinary temperatures, began immediately to liquefy, and considerable heat was evolved, while large amounts of hydrochloric acid gas were given off, indicating that the reaction was one of substitution and not addition. The color of the liquid, at first of a light straw tint, gradually grew darker as the action of the chlorine progressed. After the absorption of a considerable amount of chlorine, the straw-colored liquid possesses interesting fluorescent properties, the reflected rays being of a deep blue color. This property is gradually lost as the operation continues, and disappears completely at the point of complete saturation. The liquid contents of the tube possessed at first the consistency of rich cream. As the absorption progressed the fluidity diminished, until towards the end it was necessary to keep the U tube in boiling water in order to permit the passage of the chlorine gas. By this means the hydrochloric acid formed in the reaction was likewise completely driven off.

The product of this chlorination is a light brown syrup which at 12° is so viscous that it can be poured only with difficulty, while at 25° it is quite liquid. It is by no means stable. In contact with water or when slightly moist it decomposes very rapidly, and even when tightly corked in a perfectly dry bottle, a slow decomposition accompanied by an evolution of hydrochloric acid gas is maintained. During this process of alteration the color changes to a dirty white, beginning at the surface and gradually extending throughout the mass. It is entirely insoluble in water,

but dissolves readily in hot alcohol, ether, benzene, and carbon disulphide. Attempts were made to obtain crystalline products from the various solutions, but without success. The specific gravity was found to be 1.43 at 17°. When heated on porcelain it becomes quite fluid; white fumes and, later, dark fumes without acid reaction are given off. It burns, but is incapable of continued combustion unless kept close to a flame. When exposed to distillation hydrochloric acid vapors are first given off, and then heavy white non-condensible vapors are evolved in company with liquid distillates. Each successive series of distillations gives products of lighter color and a less viscous nature. No considerable fractions of fixed boiling point could, however, be isolated.

Although the nature of this product was not such as to offer much hope of its being a well defined compound in a state of purity, it was submitted to analysis with the following results:

I. 0.7755 gram of substance, after combustion with lime, gave 1.3757 grams of silver chloride, equal to 0.3403 gram of chlorine, or 43.88 per cent.

II. 0.6657 gram of substance gave 1.1714 grams of silver chloride, equal to 0.2897 gram of chlorine, or 43.53 per cent.

III. 0.5387 gram of substance gave 0.9308 gram of silver chloride, equal to 0.2302 gram of chlorine, or 42.74 per cent.

These analyses were made in succession, the first immediately after the preparation of the substance, the others at intervals of three days. The constant diminution of the percentage of chlorine shows the rapidity of decomposition.

IV. 0.3341 gram of substance gave on combustion with lead chromate 0.653 gram of CO_2, equal to 0.1781 gram of C, or 53.31 per cent.; and 0.0842 gram of H_2O, equal to 0.0093 gram of H, or 2.8 per cent.

	Found.	Calculated for $C_{13}H_7Cl_3$.
C	53.31	55.92
H	2.80	2.72
Cl	43.88	41.36
	99.99	100.00

The composition approximates to that of a trichloracenaphthene, and the analytical results are only of value as showing that that compound would probably represent the limits to be reached by the direct chlorination of acenaphthene at temperatures below 100°.

XL.—ON THE URANATES OF AMMONIUM AND OF CERTAIN AMINES.

By A. I. Carson and T. H. Norton.

The literature of uranium shows that uranates of the metallic bases of normal composition, with the exception of the potassium, sodium, and lithium uranates, as prepared by the ingenious method of Zimmermann,[1] are exceedingly rare. The analyses almost invariably show more or less notable deviations in the amount of uranium present from that prescribed by theory. These deviations are in the case of the ammonium salt 1.5 per cent., barium salt 1.2 per cent., lead salt 1 per cent., and silver salt 3 per cent., while in all other cases there is not even an approximation to the theoretical composition.

The following preparations were made in the view of ascertaining the possibility of obtaining salts of more normal composition with representative organic bases.

Ammonium Uranate.—We deemed it well in this connection to first prepare and analyse this salt before passing to the study of the compounds with the substituted ammonias. Two samples were prepared, both by the addition of ammonia to an aqueous solution of uranium nitrate. The light yellow precipitate, which forms at once, was thoroughly washed and dried at 100°. The analysis of this salt, as well as of the other salts to be described, was exceedingly simple. Weighed amounts of the salt dried to constant weight at 100° were gently ignited, and changed into the green oxide of uranium, U_3O_8. In a few cases, which will be noted, the black oxide of uranium, UO_3, was obtained. (The first mentioned contains 84.9 per cent. of uranium, the second 85.7 per cent.)

Analyses:

	Calculated for $(NH_4)_2U_2O_7$.	Found. First Sample. I.	II.	Second Sample.
U	76.43	72.90	72.92	74.19

The results show not only an abnormal but also variable composition. Peligot found 75 per cent. of uranium in a sample of this salt.

Uranates of the Amines of the Fatty Series.—In their preparation the amines, either in the pure state or in 33 per cent. aqueous solution, were added to the aqueous solution of uranium nitrate.

[1] Ann. Chem. (Liebig) **213**, 291.

The precipitates obtained were amorphous, insoluble, of a sticky gelatinous nature, and ranged in color from light yellow to orange. They were thoroughly washed by decantation and filtration, dried to constant weight at 100°, and analysed by the same method as given in the case of ammonium uranate. During desiccation the color always deepened. When dry they could easily be powdered.

Methylamine Uranate.—The color is of a bright canary yellow. Two different samples were prepared. The analyses gave:

	Calculated for $U_2O_7(NH_2CH_3)_2$.	Found in Samples. I.	II.
U	73.17	74.13	72.54

Variable and abnormal composition was also here evident. Ignition of the first sample gave the black oxide, of the second the green oxide.

Dimethylamine Uranate.—Color a bright canary yellow. Two analyses were made from the same preparation. Each gave on ignition the green oxide.

	Calculated for $U_2O_7[NH_2(CH_3)_2]_2$.	Found. I.	II.
U	70.17	74.27	74.25

The abnormal composition is quite evident.

Trimethylamine Uranate.—Same color as the preceding compound. Two analyses were made from the same preparation. In each case the green oxide was obtained.

	Calculated for $U_2O_7[NH(CH_3)_2]_2$.	Found. I.	II.
U	67.41	71.23	71.11

The discrepancy is here still more striking.

Ethylamine Uranate.—The color is a yellowish orange. Two analyses were made of the same preparation. The black oxide was obtained in each case.

	Calculated for $U_2O_7(NH_2C_2H_5)_2$.	Found. I.	II.
U	70.17	69.90	70.17

This is the only case in which a practically normal salt was obtained.

Diethylamine Uranate.—The color was light orange. Two analyses of the same preparation gave:

	Calculated for $U_2O_7[NH_2(C_2H_5)_2]_2$.	Found. I.	II.
U	64.86	61.21	61.24

The black oxide was obtained in each case. The variation is marked.

Triethylamine Uranate.—Yellowish brown color. Two analyses of the same preparation gave:

	Calculated for $U_2O_7[NH(C_2H_5)_3]_2$.	Found. I.	II.
U	60.30	63.13	62.60

The black oxide was obtained in each case. Variation as in the preceding case.

Isobutylamine Uranate.—Color light orange. Two preparations were made. The analyses gave:

	Calculated for $U_2O_7(NH_3C_4H_9)_2$.	Found. Sample 1. I.	Sample 2. II.	III.
U	64.86	69.41	72.57	71.88

This salt shows the most striking case of abnormal and variable composition. The first sample gave the black oxide, the second the green oxide on ignition.

As will be seen from the above analytical results, the uranates of the amines of the fatty series can, as a class, lay but little claim to normal or constant composition; the greatest variations being noted in the compounds containing the largest amount of carbon.

Uranates of the Aromatic Amines.—While the addition of aromatic amines causes a precipitation in solutions of uranium nitrate, the products thus obtained seem to be of an exceedingly unstable nature, decomposition setting in almost immediately on precipitation. Three preparations of an aniline salt were attempted. In the first case aniline was added to an aqueous solution of uranium nitrate; in the other two cases it was added to an ethereal solution of the salt dried over calcium chloride. All three products resembled in color ordinary green uranium oxide. The analyses of the three samples gave:

	Calculated for $U_2O_7(NH_3C_6H_5)_2$.	Found. I.	II.	III.
U	61.54	78.56	40.27	51.41.

The first preparation gave on ignition the green oxide, the other two the black oxide. Toluidine gave equally unsatisfactory results.

XLI.—ON SOME NEW NITROPRUSSIDES.

By T. H. Norton.

The two following salts have been prepared and studied in this laboratory by Carrie E. Joslin.

Cadmium Nitroprusside, $CdFeCy_5NO$.—This salt is obtained in the form of an amorphous flesh-colored powder on the addition of cadmium nitrate solution to a concentrated solution of potassium nitroprusside. It is insoluble in water; concentrated hydrochloric acid dissolves it readily, yielding a garnet-colored solution. Long continued boiling with both dilute and concentrated nitric acid does not affect it. It is likewise not attacked by ammonia or caustic alkalies. Exposure to light and air causes no perceptible change. It possesses a specific gravity of 2.06 at 17° and is decomposed at 290°. The analysis was made by decomposing with boiling sulphuric acid, estimating the cadmium as cadmium sulphide, and estimating the iron as ferric oxide.

I. 0.8109 gram of the salt dried to constant weight at 115° gave 0.3083 gram of CdS, equal to 0.312 gram of Cd, or 34.33 per cent.; and 0.1928 gram of Fe_2O_3, equal to 0.135 gram of Fe, or 16.65 per cent.

II. 1.0353 grams of the salt dried to constant weight at 115° gave 0.4528 gram of CdS, equal to 0.3522 gram of Cd, or 34.02 per cent.; and 0.2491 gram of Fe_2O_3, equal to 0.1744 gram of Fe, or 16.85 per cent.

	Calculated for $CdFeCy_5NO$.	Found. I.	Found. II.
Cd	34.12	34.33	34.02
Fe	17.06	16.65	16.85

Mercurous Nitroprusside, Hg_2FeCy_5NO.—This compound is obtained in the form of a pink-colored amorphous precipitate on adding a solution of mercurous nitrate to a solution of potassium nitroprusside. Its specific gravity is 3.9 at 17°. It is far from stable, being gradually decomposed by the action of air and of light. At 90° it assumes a grayish color, and at 120° it becomes perfectly black.

The method of analysis was similar to that of the cadmium salt.

I. 0.3435 gram of the salt dried to constant weight at 40° gave 0.2579 gram of HgS, equal to 0.2223 gram of Hg, or 64.71 per cent.; and 0.046 gram of Fe_2O_3, equal to 0.0322 gram of Fe, or 9.37 per cent.

	Calculated for Hg_2FeCy_5NO.	Found.
Hg	64.93	64.71
Fe	9.08	9.37

The following two salts have been prepared and examined by C. F. Windisch:

Cobalt Nitroprusside, $CoFeCy_5NO$.—This salt was precipitated on the addition of cobalt sulphate solution to a concentrated solution of sodium nitroprusside in the form of a finely divided, almost crystalline powder of a delicate pink color. The salt thus obtained is in a hydrated form and loses its water at 105°, assuming a deep blue tint. It is, however, extremely hygroscopic in this state, and rapidly absorbs moisture on cooling, resuming the original pink color. It is entirely decomposed at 170°. The compound is quite unstable, and for this reason, as well as on account of the hygroscopic nature of the anhydrous salt, it was impossible to obtain perfectly satisfactory analytical results. Two water determinations made by heating the salt dried at 40° to 105° gave 18.98 and 18.79 per cent. of H_2O. The formula $CoFeCy_5NO + 4H_2O$ would require 20.7 per cent.

An analysis of the anhydrous salt, made as soon as possible after its preparation, gave:

	Calculated for $CoFeCy_5NO$.	Found.
Co	21.40	23.37
Fe	20.38	23.20

Decomposition proceeds very steadily, as shown by the following analyses made at successive intervals of a week:

	I.	II.	III.
Co	26.20	28.62	30.06
Fe	24.66	28.19	29.44

Nickel Nitroprusside, $NiFeCy_5NO$.—The preparation of this salt is similar to that of the cobalt salt. It is obtained in the hydrated form as a dirty gray powder. Constant water determination could not be obtained. At 105° it loses water and assumes a dark green color. The anhydrous salt absorbs moisture with avidity and resumes its original gray color. At 160° complete decomposition occurs. Under ordinary circumstances decomposition likewise takes place, and analytical results were rendered unsatisfactory from this cause and from the extreme hygroscopic nature of the anhydrous salt. An analysis made shortly after the preparation gave:

	Calculated for $NiFeCy_2NO$.	Found.
Ni	21.40	19.83
Fe	20.38	19.53

An analysis made a few weeks later gave:

Ni	24.48
Fe	23.25

XLII.—ANALYSIS OF LOCKPORT SANDSTONE.

By H. W. Weld.

The so-called Medina sandstone has long enjoyed a high reputation as a building stone on account of the fineness of its texture and the delicacy of its coloring, qualities which have led to its use in the construction of prominent structures in many parts of the country. I am indebted for a sample of this sandstone to the courtesy of Mr. Charles Whitmore, proprietor of the important quarry at Lockport, N. Y., where the choicest varieties of the Medina stratum are obtained.

The analysis yielded the following results:

	I.	II.
SiO_2	96.31	96.52
Fe_2O_3	0.70	0.70
Al_2O_3	1.71	1.60
CaO	0.99	1.05
	99.71	99.87

No moisture was present.

The high percentage of silica and the small amount of cementing material are worthy of note as of comparatively rare occurrence. Bornemann[1] found sandstones in the Hartz mountains containing from 96.68 to 98.47 per cent. of silica. Haas[2] gives analyses of Bohemian sandstones containing from 90.55 to 93.33 per cent. of silica. Other recorded analyses of sandstones approaching so nearly the composition of pure quartz are exceedingly rare.

[1] Jahrbuch der Mineralogie, 1852, 1. [2] Wien. Acad. Ber. (2 Abtheil.) **61**, 763-764.

Contributions from the Chemical Laboratory of the University of North Carolina.

Reported by F. P. VENABLE.

ACTION OF CHLOROUS ACID UPON HEPTYLENE.

BY ROBT. G. GRISSOM.

The heptane from Pinus Sabiniana has been shown by Schorlemmer to be probably a normal heptane. The heptylene used in the following experiments was prepared from this heptane by first brominating it and then acting upon the secondary bromide formed with sodium ethylate. It was found that the best results were secured by allowing the sodium ethylate to act from twelve to twenty-four hours in the cold, and then distilling off the heptylene and alcohol together. The end of the condenser tube may dip underneath water, or better, end just above the surface of it, thus separating the alcohol from the heptylene. The latter does not seem to be soluble in water to any great extent. This heptylene was dried, redistilled, and the portion boiling at 98°–100° was used for the experiments.

The chlorous acid was formed by the action of sulphuric acid, diluted with two parts of water, on a mixture of potassium chlorate with half its weight of oxalic acid. The stream of chlorous acid mixed with carbon dioxide, thus produced, was then led into the tube containing the heptylene. To start the evolution of the gases, the small flask containing potassium chlorate and oxalic acid mixed with sulphuric acid was gently warmed by placing it in warm water. Application of cold water was used to moderate the action when necessary. Only ten or fifteeen grams of potassium chlorate were used at one time. Following the directions of Domac,[1] the heptylene (about 110 grams) was placed in four tall test tubes so that each was about half full. These were properly connected with the flask for generating the gases and were surrounded by ice-water. The gas delivering tube ended just above the surface of the heptylene, thus adopting Domac's precaution, so as to avoid the troublesome explosions. To make the absorption as regular as possible, the position of the tubes with reference to the generating flask was regularly changed. The absorption was rapid, the

[1] Ann. Chem. **213**, 125.

heptylene going through various changes of color from yellow to a deep orange-brown. When the deeper color was reached the tubes were disconnected from the generating flask and placed in direct sunlight until the orange color was lost. If taken from ice water the heptylene became very warm and a rapid evolution of gas took place. It was much the best, and tended to prevent a complication of reactions, to keep the tubes all the time at a low temperature, and to shade them even from sunlight during the passage of gas. After several days the absorption took place more slowly, and an exposure of many hours was needed for decolorisation. Even with great care explosions would take place after the heptylene was largely saturated with the gas, and about half of the heptylene was thus lost. It was necessary then to stop before complete saturation or a permanent coloration was reached. The oily liquid was thoroughly washed with water until the washings no longer had an acid reaction. This wash-water acquired a pungent, irritating odor. The remaining oil was dried over calcium chloride.

Aqueous Solution.—On examining first the water used in washing it was found strongly acid; still but little of the original liquid seemed to have gone into solution. A portion of the water was placed over sulphuric acid and on evaporation left a small residue, white, deliquescent, and somewhat oily. The main part was apparently crystallised, contained chlorine, and had the smell of acetic acid and its chlorine derivatives. The amount obtained was too small for purification or further attempt at identification. The remainder of the solution was neutralised with barium carbonate, changing from a clear liquid to a rosy flesh color. The same fruity, pungent, irritating odor was noticed. This was filtered, and after evaporation to a small bulk, the barium precipitated by sulphuric acid. After filtering again it was distilled. Three fractions were taken. The first, under 100°, gave no test for chlorine; the second, 100°–101°, contained chlorine; the third, 101°–110°, contained both chlorine and sulphuric acid, the latter coming from the slight excess used in precipitating the barium. As the first only gave promise of interesting results, it was saturated with Ag_2O, filtered, evaporated over sulphuric acid, and the thin crystalline film left was analysed. As the amount of silver found was within two per cent. of that required by silver acetate, it was concluded that the principal acid present in the aqueous solution was acetic acid. The presence of chlorine, sulphuric acid and oily impurities prevented

an examination of the other fractions for butyric or other acids, and the amount was too small to attempt to purify them.

The Oil insoluble in Water.—The oily portion after the washing and thorough drying over calcium chloride, was subjected to fractional distillation under diminished pressure. In this fractionation that part boiling below 120° was looked upon as mainly unchanged heptylene. The fraction from 120°–160° was set aside. It contained chlorine, and after attempts at reduction persistently retained it. The remaining portion was fractionated three times, yielding fractions as follows: A, 160°–173°; B, 173°–177°; C, 177°–185°; D, 185°–200°; and E, over 200°. This last fraction was quite small, the thermometer rising rapidly until only a few drops remained. None of these fractions were more than a few cc. in amount. All were at first clear, colorless liquids, but the last two rapidly darkened, even though in sealed tubes and carefully secluded from the light. Fraction B was the largest in amount (6–7 cc.), and as the thermometer rose slowly from 173°–177°, this was supposed to be the purest substance, or the nearest approach to a single chemical individual. As stated before, it was the result of three careful fractionations. It was subjected to the first and most complete examination. All of the temperatures by which these fractions are distinguished are subject to correction, due to the pressure being reduced by 100 mm. The following analyses were made of these respective fractions.

Fraction B, 173°–177°.

I. 0.3170 gram substance gave 0.2205 gram H_2O, and 0.6300 gram CO_2; or 7.73 per cent. H, and 54.19 per cent. C.

II. 0.3203 gram substance gave 0.2547 gram H_2O, and 0.6336 gram CO_2; or 8.83 per cent. H, and 53.94 per cent. C.

III. 0.4181 gram substance gave 0.3287 gram H_2O, and 0.8268 gram CO_2; or 8.73 per cent. H, and 53.93 per cent. C.

IV. 0.2785 gram substance gave 0.3139 gram AgCl; or 27.85 per cent. Cl.

V. 0.2750 gram substance gave 0.3043 gram AgCl; or 28.05 per cent. Cl.

Fraction C, 177°–185°.

VI. 0.3259 gram substance gave 0.2575 gram H_2O, and 0.6544 gram CO_2; or 8.78 per cent. H, and 54.77 per cent. C.

Fraction D, 185°–200°.

VII. 0.2642 gram substance gave 0.2087 gram H_2O, and 0.5402 gram CO_2; or 8.78 per cent. H, and 55.79 per cent. C.

Fraction E, above 200°.

VIII. 0.3165 gram substance gave 0.2513 gram H_2O, and 0.6567 gram CO_2; or 8.81 per cent. H, and 56.27 per cent. C.

IX. 0.2260 gram substance gave 0.1794 gram H_2O, and 0.4672 gram CO_2; or 8.82 per cent. H, and 56.38 per cent. C.

X. 0.2680 gram substance gave 0.255 gram AgCl; or 23.49 per cent. Cl.

The following table will show how these percentages compared with those calculated for the chlorine compounds, which suggest themselves as possibly formed during the reaction:

	B.	C.	D.	E.	$C_7H_{13}ClO$.	$C_7H_{14}Cl_2O$.	$C_7H_{14}Cl_2$.
H	8.83	8.78	8.78	8.82	8.76	7.57	8.29
C	53.94	54.77	55.79	56.38	56.60	45.45	49.76
Cl	27.85	...	...	23.49	23.85	38.31	41.94

It will be observed that while the percentage of hydrogen is about the same throughout, the percentage of carbon increases up to the last fraction E. This one approaches in all of its percentages very nearly to $C_7H_{13}ClO$. That it is free from impurity is hardly possible, as is shown by the inconstant boiling point. As to the nature of the more highly chlorinated body or bodies with which it is mixed, nothing can be determined by the analyses. From the great difficulty with which chlorine was removed, it is most probable that simple chlorides were present. Nitric acid caused complete decomposition only in the neighborhood of 200°, and nascent hydrogen failed to act. As the nature of the reduction products would throw some light on the composition of these fractions, their reduction was attempted. First iron filings and acetic acid were used, then sodium amalgam, but the chlorine was not entirely removed even after days of action. The small amounts experimented with rendered vain any attempt at separation by distilling.

To sum up the results of the action of chlorous acid upon heptylene from Pinus Sabiniana, we find acetic acid and some chlorinated solid acid formed by the oxidising action, but the main portion changed into a chlorhydrine, mixed probably with chlorides.

The ease of decomposition of the chlorous acid renders it hardly possible to limit the nature of the reaction and prevent its becoming very complex.

NEW HALOGEN COMPOUNDS OF LEAD.

Lead chlorosulphocyanide. (By R. G. GRISSOM.)—This new compound can be easily prepared by acting on lead chloride with a strong solution of potassium sulphocyanide. Freshly precipitated and recrystallised lead chloride was covered with a solution of potassium sulphocyanide in excess and allowed to stand for several days. The liquid was then poured off and the residue heated several times with boiling water until all was dissolved. This fractional solution was carried out to separate, if possible, substances of different solubility. The fractions rapidly deposited crops of crystals on cooling, but examination under the microscope showed that these crystals were identical in form. Analyses were made as follows:

0.6220 gram of substance gave 0.5730 $PbSO_4$, or 68.57 per cent. of Pb. 1.0280 grams of substance gave 0.7047 gram $PbSO_4$, or 68.55 per cent. Pb.

For chlorine and sulphocyanic acid 1.0700 grams of the substance were dissolved in water and precipitated with silver nitrate. This was filtered and treated with strong nitric acid, thus oxidising the sulphocyanide. After dilution it was again filtered. The silver chloride was burned and the sulphuric acid determined in the filtrate in the usual way.

1.0700 grams of substance yielded 0.1321 gram of AgCl, or 12.34 per cent. Cl; and 0.8440 gram $BaSO_4$, or 19.62 per cent. CNS.

	Calculated.	Found.	
Pb_2	68.46	68.57	68.55
Cl_2	11.91	12.34	
$(CNS)_2$	19.41	19.63	

The formula for the compound then is $PbCl_2.Pb(CNS)_2$. There is no water of crystallisation, and the substance can be heated to 150° without decomposition.

The solution poured off from the original lead chlorosulphocyanide yielded mainly crystals of potassium chloride together with some unchanged potassium sulphocyanide. The potassium sul-

phocyanide was freshly prepared and purified by frequent recrystallisation.[1]

Action of ammonium hydroxide upon lead chlorosulphocyanide.—Crystals of this salt, dried at 100° and kept several months, turn partially yellow from the formation of persulphocyanogen. Those merely dried in the air do not seem to undergo this change. Some of these air-dried crystals were covered with ordinary aqua ammonia in excess and allowed to stand for six days. The color of the crystals was slightly changed, becoming dirty yellowish white. On analysis, after drying at 100°, they were found to contain 3.08 per cent. of chlorine. Sulphocyanic acid was also present, but was not determined. Another lot, after standing for three hours, gave 5.28 per cent. of chlorine. Crystals covered in the same way with ammonia water and boiled occasionally during six hours showed on analysis 2.76 per cent. of chlorine, and gave qualitative tests for sulphocyanic acid. Others boiled in this way during three or four weeks gave but a bare opalescence with silver nitrate. Ammonium hydroxide, then, does not remove either of the radicals combined with the lead in preference to the other, but removes both at the same time, until only lead hydroxide is left. Nor do there seem to be any distinct steps of removal or regular basic compounds formed as in the case of the action of ammonium hydroxide on lead chloride and iodide.[2]

Lead bromosulphocyanide.—Lead bromide crystallised from a strong solution of potassium sulphocyanide gave slightly brownish crystals, apparently of the first system. These were dried on filter paper and then over sulphuric acid. They contained 23.05 per cent. of bromine and 16.65 per cent. CNS. Calculated for PbBrCNS, 23.02 per cent. bromine and 16.85 per cent. CNS.

Hydrobromic acid was added to the mother-liquor of these crystals, and on evaporation a crop of clumpy, indistinctly yellowish crystals was obtained. These were dried and analysed, giving 3.46 per cent. of CNS. Calculated 3.56 per cent. of CNS for $8PbBr_2 . Pb(CNS)_2$.

Lead iodosulphocyanide. (By B. THORP.)—The first attempt at preparing this salt was by adding the excess of potassium sulphocyanide, in solution, to freshly precipitated lead iodide. On washing

[1] As Mr. Grissom was forced to leave the work at this point and it could not be turned over to any other student in the laboratory just then, I undertook myself the examination of this and other lead compounds. A description of this work follows.

[2] Chemical News 52, 43.

with hot water lead iodide alone crystallised out. Again sulphocyanic acid was used to dissolve lead iodide, but the double compound refused to form and again the iodide only crystallised out. When equivalent amounts of lead iodide and lead chlorosulphocyanide were dissolved in boiling water and allowed to crystallise, the iodide crystallised out by itself. Lastly, lead iodide was dissolved in a strong solution of potassium sulphocyanide. This gave on cooling small glistening nearly white crystals. It is interesting to note in this and other cases where double compounds with lead iodide were obtained, that at one stage of the cooling numbers of large, distinct crystals of lead iodide would separate. On further standing and cooling these would entirely disappear and all the crystals would be of the double compound.

Analysis gave for this compound figures corresponding to 57.22 per cent. Pb. Calculated for $PbI_2.3Pb(CNS)_2$, 57.83 per cent. Pb.

Lead chlorocyanide.—When lead chloride crystals were covered with a strong solution of potassium cyanide, a heavy and quite insoluble body was formed which, on standing, rapidly changed in color to a purplish brown. This was due to partial decomposition and loss of hydrocyanic acid.[1] This heavy insoluble powder was washed and then dried at 100°. The analyses gave the following results, the CN being found by difference:

	Calculated for $2Pb(CN)_2.PbCl_2$.	Found.		
Pb	77.98	78.46	78.32	77.98
Cl	8.76	8.29	8.47	8.76
CN	13.22	13.25	13.21	13.22

Lead ferrocyanide could not be induced to crystallise with lead chloride. It is so insoluble that few of the methods of formation used in this research could be put into practice. On covering lead chloride with a solution of potassium ferrocyanide, the lead gave up its chlorine completely. The resulting lead ferrocyanide persistently retained some potassium ferrocyanide. Again, when lead ferrocyanide was boiled for some time with potassium chloride, neither filtrate nor residue contained the desired double salt.

Lead ferrocyanide covered with ammonia water for several weeks yields a brownish-gray white mass which was free of ammonia and contained 12.42 per cent. of ferrocyanic acid and .45 per cent. of ferric oxide. It is a basic ferrocyanide.

[1] Chemical News 51, 45.

Of course the attempt to crystallise lead ferrocyanide from hydrochloric acid ended in the decomposition of the ferrocyanide with the formation of lead chloride and separation of Prussian blue.

Lead bromiodide. (By B. THORP.)—When lead iodide is dissolved in hydrobromic acid, the first crystals are of a deep yellow tint, approaching orange. The crystals on analysis yielded 49.75 per cent. Pb. Calculated for $PbBr_2.PbI_2$, Pb = 49.93 per cent. These crystals then have the composition represented by the formula $PbBr_2.PbI_2$.

The second crop of crystals have a straw-yellow color and gave 52.99 and 52.57 per cent. Pb, 30.61 per cent. Br, and 16.20 per cent. I. Calculated for $3PbBr_2.PbI_2$, 52.94 per cent. Pb, 30.77 per cent. Br, and 16.32 per cent. I.

The third crop are white in color and yield on analysis 54.19 and 54.34 per cent. Pb. The calculated percentages for a substance of the composition $6PbBr_2.PbI_2$ are = 54.34 per cent. Pb.

The fourth crop are also white, and gave only a slight reaction for iodine. They contained 56.12 per cent. Pb, and are therefore nearly pure lead bromide. In form these crystals are all alike, closely resembling ordinary lead bromide.

Lead chlorobromiodide. (By B. THORP.)—Lead chloride, lead bromide and lead iodide were dissolved together in hot water and allowed to crystallise. No special proportions were taken, though in the first experiment an excess of lead iodide was probably present. In the second, more lead bromide and lead chlorine were present, with the bromide probably in excess. In both cases the iodide crystallised out abundantly immediately on cooling. The second, third and fourth crops of crystals were taken separately. They were like one another in appearance, forming masses of long silky yellowish white needles. They combined chlorine, bromine, and iodine. Analyses of the three last fractions in the second experiment gave the following percentages of lead:

I. Pb = 60.34; II. Pb = 61.48; III. Pb = 61.32. Analysis of the fourth fraction gave, IV. Pb = 61.57.

There seems to be only one compound formed, as in I. the analysis was probably defective.

From these experiments it is evident that lead has quite a facility for forming double compounds with the halogens and analogous radicals, forming probably in many cases a series of such salts with various ratios between the halogens, all being quite stable and crystallising nicely.

SOME NEW SALTS OF CAMPHORIC ACID.

Although this acid has been known for over one hundred years, comparatively few of its salts have been prepared and studied. The present work was undertaken with a view of extending this list. The camphoric acid was prepared according to the directions of Wreden, by dissolving 150 grams of camphor in 2 litres of nitric acid, sp. gr. 1.27, and heating the solution 50 hours on the water-bath. The liquid was then saturated with sodium hydroxide, filtered, neutralised with hydrochloric acid, and the separated camphoric acid purified by crystallising from water. The yield was about the same as that obtained by Wreden, when great care was exercised in the purification by crystallising from water. The pure crystals gave the melting point 176° C. (uncorrected). A ten per cent. solution of caustic potash was saturated with camphoric acid, and solution of potassium camphorate so obtained was used in preparing the other compounds.

Manganese Camphorate (I. H. MANNING).—When a few drops of potassium camphorate were added to a nearly saturated solution of manganese sulphate in a small watch-glass, no precipitate was formed until heated on the water-bath. A white precipitate was then gotten which was easily soluble in cold water. This could always be reprecipitated on heating. In preparing this salt on a larger scale the mixture of potassium camphorate and manganese sulphate was heated to precipitation and the precipitate well washed with hot water. The precipitate was then dried at 100° C. If exposed in a moist condition it turned brown. There was a slight discoloration even when dried rapidly. At 150° decomposition was very slight; at 200° it was marked. When some of the manganese camphorate was dissolved in water and evaporated over sulphuric acid, a crust of the salt was obtained, but no crystal.

Analysis. (Three different preparations were used):

I. 0.2790 gram of substance gave 0.0859 gram Mn_3O_4.

II. 0.4460 gram of substance gave 0.1330 gram Mn_3O_4.

III. 0.4375 gram of substance gave 0.1330 gram Mn_3O_4.

I and III were determined by precipitating as carbonate, II by ignition.

	Calculated for $MnC_{16}H_{14}O_4$.	Found.		
		I.	II.	III.
Mn	23.07	22.07	21.39	22.50

As it was very difficult to wash away all of the potassium camphorate, the low results are probably due to the same as an impurity.

Chromium Camphorate (I. H. MANNING).—On adding potassium camphorate to a solution of chromium sulphate, a heavy precipitate of a bluish-green color is formed. This is not very soluble and can be thoroughly washed with cold water. It can be dried at 100° C., losing all water at this temperature. Before reaching 150° slow decomposition sets in.

Analysis:

I. 0.4280 gram of substance gave on ignition 0.0859 gram Cr_2O_3.

II. 1.6370 grams of substance gave on ignition 0.1340 gram Cr_2O_3.

	Calculated for $Cr_2(C_{10}H_{14}O_4)_3$.	Found. I.	Found. II.
Cr	14.81	12.93	14.40

The sample in I was different from that in II, and evidently not so pure.

Ferric Camphorate (I. H. MANNING).—A strong solution of ferric chloride was precipitated with potassium camphorate; a bulky yellowish precipitate was formed, quite insoluble in water and hence easily washed. This gave on drying at 100° a buff yellow powder. An analysis of this powder gave the percentage of iron as 19.34. The calculated percentage for $Fe_2(C_{10}H_{14}O_4)_3$ is 15.86. This powder was then probably a subcamphorate. It was treated once more with a strong solution of ferric chloride and again thoroughly washed. Analysis of this gave Fe = 18.84 and 18.90 per cent.

Mercuric Camphorate (I. H. MANNING).—A white heavy precipitate is formed on adding potassium camphorate to a concentrated solution of mercuric chloride. This was washed thoroughly and dried at 100° C. It forms a heavy white powder.

Analysis:

I. 0.4400 gram of substance yielded 0.2150 gram Hg.

II. 0.3840 gram of substance yielded 0.1920 gram Hg.

	Calculated for $Hg.C_{10}H_{14}O_4$.	Found. I.	Found. II.
Hg	50.25	48.86	50.00

Aluminium Camphorate (G. W. EDWARDS).—Pure aluminium hydroxide was prepared, and this was then boiled with camphoric

acid in excess, using only a little water. The resulting aluminium camphorate is white and quite insoluble. It was dried at 100° and analysed.

	Calculated for $Al_3(C_{10}H_{14}O_4)_3$.	Found. I.	Found. II.
Al	8.33	8.16	8.24

Nickel Camphorate (G. W. EDWARDS).—Pure nickel hydroxide was prepared and dissolved in camphoric acid, using as little water as possible. On heating this solution on the water-bath a crust, whitish-green in color, settled out. This was dried between bibulous paper and analysed.

Analysis:

	Calculated for $Ni(C_{10}H_{15}O_4)_2$.	Found.
Ni	12.76	12.03

The liquid poured off from this crust stood some days over sulphuric acid. A further settling out of the crust mentioned above was noticed; then small green crystals began to form. The liquid was filtered away from the crust and once more placed in the desiccator. The crystals obtained were dried on bibulous paper and analysed. It was impossible, however, to separate them from the crust. The analysis gave 12.50 per cent. of Ni. Hence the compound was the same as above.

Strontium Camphorate (G. W. EDWARDS).—Strontium carbonate is but slightly attacked by camphoric acid in the cold. On heating with water the evolution of carbon dioxide is rapid. The resulting strontium camphorate is soluble in water. Clusters of crystals are easily gotten on evaporation over sulphuric acid. The first analysis of the crystals was lost. Analysis of a crystalline crust resulted as follows:

	Calculated for $SrC_{10}H_{14}O_4.6H_2O$.	Found.
Sr	22.23	21.50
H_2O	27.45	27.75

DECOMPOSITION OF POTASSIUM CYANIDE.

BY I. H. MANNING.

Under the head of "Condensation der Blausäure," v. der Pfordten discusses[1] the discoloration produced in solutions of potassium cyanide by the addition of free acids or of certain

[1] Ber. d. chem. Ges. **18**, 1875.

salts, or by the simple heating of the cyanide alone. This phenomenon was examined and studied to some extent by Mr. Wilkes[1] in this laboratory. Herr v. der Pfordten speaks of the decomposition of the cyanide, on heating some hours in a test tube placed in a water-bath, as being due "probably to the long continued action of the carbon dioxide of the air." That this could not be the case was shown by Wilkes, who proved that the decomposition took place in the cold with all carbon dioxide carefully excluded. The following experiments were undertaken to test the conclusion of Mr. Wilkes:

1st. A saturated or nearly saturated solution of pure potassium cyanide was placed in a tube, which was then sealed. Only a very minute amount of carbon dioxide could have been present, yet the usual changes of color indicating the decomposition were observed, and after some weeks the liquid had become black and a blackish deposit had formed.

2d. A similarly prepared tube, sealed, was placed in boiling water. Within five minutes a change to brownish-red was noticed and the color rapidly darkened.

3d. A similarly prepared tube was fitted with cork and tubes, and while it was in boiling water, carbon dioxide was passed over the surface of the liquid. The changes were very much as in experiment 2d. Apparently they were slightly delayed rather than hastened.

4th. Into a tube prepared as in 3d, hydrogen was passed in a rapid, continuous stream. The changes were decidedly delayed, and no very deep discoloration was obtained.

5th. If experiment 3d is reversed so that the carbon dioxide is passed above a cold solution of the cyanide, giving opportunity for its absorption, the change of color is of course rapid and deep.

From these experiments the conclusion can be drawn, that though carbon dioxide hastens the decomposition of the cyanide, as any free acid would do, yet it is not essential that it should be present, and in many cases the decomposition cannot be attributed to it, as is done by v. der Pfordten. It would seem that the decomposition was spontaneous, or, at most, assisted by the presence of traces of organic matter.

[1] Chemical News 51, 45.

ON THE BROMINATION OF HEPTANE.

By F. P. Venable.

Schorlemmer has shown that the heptane from *Pinus sabiniana* is probably identical with that from petroleum and is a normal heptane. With regard to the action of the halogens upon this heptane he says:[1] "By the action of chlorine upon a normal paraffin not all the chlorides indicated by theory are formed, but only the primary and a secondary chloride which contains the group $CHCl.CH_3$; by the action of bromine upon normal paraffins from petroleum only secondary bromides corresponding to chlorides are formed."

In my inaugural dissertation (Göttingen, 1881, p. 14) I stated that I found other products formed during the bromination of normal heptane besides the secondary bromide, but did not examine them more closely. It seemed to me worthy of note at the time that when the unfractionated residue boiling above 170° C. (the secondary bromide boils at 165°–167°) was allowed to stand some time and was then distilled, it yielded, under evolution of hydrogen bromide, a fair proportion of secondary bromide boiling at 165°–167°. Time and material have both been lacking to me since the period of that research, and hence I have made no closer examination of this point.

As it would be a strange and not very easily accounted for fact if bromine yielded only secondary products acting on normal paraffins, I determined to make use of a recent opportunity to examine this action more closely.

It may be stated that in several brominations of this heptane made in recent years I have found the yield of secondary bromide to be only about 25 or 30 per cent. of the theoretical, much of the heptane remaining unattacked and much having to be rejected as boiling too high. The amounts of heptane brominated at one time varied from 100 to 300 grams, and the bromine usually dropped in as fast as it could be absorbed by the hot heptane. No quantitative data were preserved of these experiments, however. The yield is seriously unsatisfactory with so expensive a material as the heptane.

The following experiments were quantitative and conducted with especial care:

[1] This Journal **6**, 31.

I. 100 *grams of pure heptane and* 160 *grams of bromine.*—The heptane was kept boiling gently over a naked flame. The flask containing it was provided with an inverted condenser and a dropping funnel for the bromine. The bromine dropped in the liquid, keeping it orange-red in color. The operation required five hours. The heavy oil was then washed with dilute sodium carbonate, then with water, and finally dried over calcium chloride. It was yellow with an orange tint. It was fractionated twice under a diminished pressure of 18–20 inches of mercury; then four times fractionated under ordinary pressure. The divisions were as follows:

Fraction I, 100°–120°, nearly all under 110°,	30 grams;
II, 120°–162°,	5
III, 162°–168°, mainly 164°–167°,	55
IV, 168°–173°,	2
V, 173°–183°, mainly between 176°–180°,	8
VI, 183°–210°,	10

Probably one fourth, in bulk, of the oil was left partly charred in the fractionating flasks.

II. 100 *grams of pure heptane and* 160 *grams of bromine.*—The same apparatus as above was used, only the dropping funnel was drawn out to a capillary and about half an inch of this was submerged under the heptane. The bromine entered thus slowly and in the form of vapor. The heptane was at first at a lower temperature than in the first experiment. The temperature had to be increased later on, but so far as possible all excess over that necessary for the absorption of the bromine was avoided. The time consumed by the reaction was about thirteen hours. The oil was then treated as above. It was redder in color. It was fractionated as above, only one time less under ordinary pressure.

Fraction I, 100°–120°, mainly under 110°,	35 grams;
II, 120°–162°,	5
III, 162°–168°, mainly 164°–167°,	25
IV, 168°–173°,	6
V, 173°–183°, mainly 176°–180°,	20

No higher fraction than V was taken, though several grams could have been gotten by carrying the residue on to partial charring. Fraction V was in this case much more stable than the correspond-

ing fraction in the first experiment. It did not turn brown so quickly, nor deposit black spots on the glass.

III. 50 *grams of pure heptane and* 80 *grams of bromine.*—No heat was used in this case. The heptane was in a small open Erlenmeyer flask which was set in a vessel of water. The bromine was poured in in small amounts and shaken until dissolved in the heptane, giving it a deep red color. Then it was allowed to stand in the light until only a yellow color remained. The temperature averaged about 6° C. The duration of the experiment was twenty-five days. The resulting oil was washed as above. It was bright yellow in color. It was fractionated once under diminished pressure and once under ordinary pressure. The following fractions were obtained:

Fraction I, 100°–120°, mainly under 110°,	12 grams;
II, 120°–162°,	2
III, 162°–173°, mainly 164°–167°,	4
IV, 173°–183°,	7
V, 183°–195°,	very little;
VI, 195°–205°,	7 grams;
VII, 205°–215°,	12
VIII, 215°–230°,	8

These fractions above 195° were heavy, of a brownish yellow color, and not showing much decomposition on standing. This third method of bromination was tried several times with similar results. Analyses of two proportions of the fraction coming over about 210° gave 56.4 per cent. and 58.0 per cent. of bromine; $C_7H_{15}Br$ contains 44.69 and $C_7H_{14}Br_2$ 62.02 per cent. of bromine.

The results may be summed up thus: If we take into consideration the boiling points of the primary bromide (178.5°), secondary bromide, 164°–167°, and dibromide or heptylene bromide, 209°–211°, it will be seen that no mode of bromination tried yielded the secondary bromide alone. The first yields principally the secondary; the second yields secondary and primary, whereas the third yields mainly compounds having a high percentage of bromine, probably several isomeric bromides of heptylene. The action of bromine then seems to be quite similar to that of chlorine.

UNIVERSITY OF NORTH CAROLINA, *February*, 1888.

REVIEWS AND REPORTS.

The Higher Oxides of Manganese, and the Acids corresponding to them.

In a late number of this Journal (9, 458) there appeared a report on "Recent advances in the chemistry of manganese," based upon the researches of Christensen and Franke. Since then another communication on this subject has come to hand, in which Franke describes certain new double salts of manganese with the alkaline sulphates, and discusses the structure of new oxides which he has obtained from these salts by very simple transformations.

The double salts, which serve as the starting points in this investigation, are all obtained from potassium permanganate and sulphuric acid. As to whether one or another of these double salts is obtained depends entirely on the concentration of the sulphuric acid, the temperature, and the amount of permanganate used. The space allotted to these reports will not permit the giving of all the details involved in their preparation, and the reader is referred to the original article.[1]

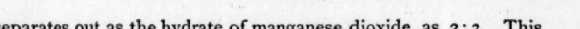
When potassium permanganate is added to concentrated sulphuric acid, a double salt of manganese and potassium having this composition, $2Mn_2(SO_4)_3 + 5K_2SO_4$, separates. This compound is obtained as a beautifully crystallised bordeaux-red salt, which dissolves in dilute sulphuric acid with a brown color, in concentrated sulphuric acid with a violet color. When heated sufficiently it decomposes into manganese sulphate, sulphur dioxide, and oxygen. When treated with a considerable quantity of water it is decomposed into manganese and potassium sulphates, the hydrate of manganese dioxide, and sulphuric acid, a decomposition which may be represented by this equation:

$$2Mn_2(SO_4)_3.5K_2SO_4 + 12H_2O = 6MnO_2\text{ (hydrate)} + 5K_2SO_4 + 4MnSO_4 + 12H_2SO_4.$$

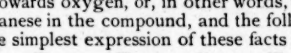
Manganous manganate, Mn_3O_4 or $3MnO_2.2MnO$.—When the double salt $2Mn_2(SO_4)_3.5K_2SO_4$ is first added to water, a compound which crystallises in glittering yellow leaflets separates. This compound, if allowed to stand in the acid liquid, soon changes to manganese sulphate and the hydrate of manganese dioxide. By rapid filtration, however, and washing with water, it is possible to obtain it in pure condition, and it is found to have the composition Mn_3O_4. When this oxide is treated with dilute sulphuric acid it breaks down, yielding manganous sulphate and manganese dioxide; and it is found further that the quantity of manganese which exists in the solution as the sulphate is to the manganese which

[1] J. prakt. Chem. **36**, 168 and 451.

separates out as the hydrate of manganese dioxide, as 2 : 3. This indicates that in the compound Mn_5O_8 the manganese exhibits two different valences towards oxygen, or, in other words, that we have two kinds of manganese in the compound, and the following structural formula is the simplest expression of these facts :



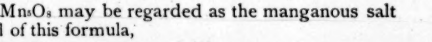
The compound Mn_5O_8 may be regarded as the manganous salt of a manganic acid of this formula,



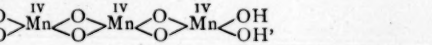
and all of the transformations of the double salt, $2Mn_5(SO_4)_8.5K_2SO_4$, can readily be explained by the aid of these formulas.

If we leave out of the equations the potassium sulphate, which after it is once split off takes no further part in the reaction, we have the decomposition of the compound, $2Mn_5(SO_4)_8.5K_2SO_4$, expressed by the following equations :

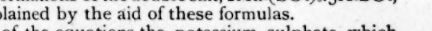
I. $Mn_5(SO_4)_8 + 4H_2O$



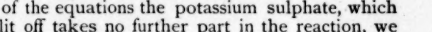
II. $Mn_5O_8 + 2H_2SO_4$



III. $3MnO_2.2H_2O + 2H_2SO_4 = 4H_2O + SO_4$

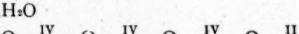


IV. $SO_4 =$

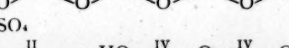


$= (MnO_2) = SO_4 + O = Mn = O + MnSO_4.$

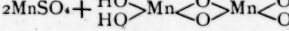
Now, just as we have an oxide, Mn_2O_5, which may be regarded as a manganous salt of a manganic acid, so we have still lower oxides in which this same relation exists. Thus the next lower member of this series would be an oxide of the formula Mn_4O_6, whose structure we may represent in this way :



This we may consider as derived from an acid,



In the same way we may have an oxide Mn_3O_3 or



which may be considered the manganous salt of the acid,

$$\begin{matrix} HO \\ HO \end{matrix}\!\!>\overset{IV}{Mn}=O.$$

Of course, another view may be taken of an oxide of the composition Mn_2O_3, and we may regard it as a sesqui-compound in which the valence of the two manganese atoms is the same; such an oxide would have this formula: $O<\begin{matrix}\overset{III}{Mn}=O \\ Mn=O\end{matrix}$.

Franke has been able to obtain several of the compounds mentioned, but in no case has he been able to obtain compounds in which the valence of all the manganese atoms is the same, and he concludes that the existence of sesqui-compounds of manganese is highly improbable, if not impossible. Franke finds that when potassium permanganate is treated with sulphuric acid under slightly varying conditions, it is possible to obtain salts of the following compositions: $Mn_2(SO_4)_3.H_2SO_4 + 4H_2O$, $Mn_2(SO_4)_3.K_2SO_4$, and $Mn_2(SO_4)_3$. When these salts are decomposed by means of water they all yield, as the chief products of the decomposition, manganese sulphate, $MnSO_4$, and the hydrate of manganese dioxide, $MnO_2.H_2O$; and in every case the quantity of the manganese which exists in the solutions as the sulphate is to that precipitated as $MnO_2.H_2O$, as 1 : 1, nearly.

This indicates that in these compounds, as in the compound $2Mn_2(SO_4)_3.5K_2SO_4$, we have two kinds of manganese; and the decompositions which these substances undergo can be best explained by these equations:

I. $$\overset{II}{Mn}<\begin{matrix}SO_4 \\ SO_4\end{matrix}\!\!>\overset{IV}{Mn}=SO_4+4H_2O$$
$$=\overset{II}{Mn}<\begin{matrix}O \\ O\end{matrix}\!\!>\overset{IV}{Mn}<\begin{matrix}OH \\ OH\end{matrix}+3H_2SO_4;$$

II. $$\overset{II}{Mn}<\begin{matrix}O \\ O\end{matrix}\!\!>\overset{IV}{Mn}<\begin{matrix}OH \\ OH\end{matrix}+H_2SO_4$$
$$=\overset{II}{Mn}SO_4+\begin{matrix}HO \\ HO\end{matrix}\!\!>\overset{IV}{Mn}=O+H_2O.$$

That the compound $\overset{II}{Mn}<\begin{matrix}O \\ O\end{matrix}\!\!>\overset{IV}{Mn}<\begin{matrix}OH \\ OH\end{matrix}$ is formed in the first stage of the above reaction is further shown by the fact that it is precipitated as such when the salt, $\overset{II}{Mn}<\begin{matrix}SO_4 \\ SO_4\end{matrix}\!\!>\overset{IV}{Mn}=SO_4$, is treated with a dilute solution of sodium carbonate.

From these reactions there can be scarcely any doubt that the compound, $Mn_2(SO_4)_3$, has the structure represented by the formula $\overset{II}{Mn}<\begin{matrix}SO_4 \\ SO_4\end{matrix}\!\!>\overset{IV}{Mn}=SO_4$, and further, since the compound, $MnCl_4$, shows similar properties and exhibits essentially the same decompositions, we cannot but assign to it a similar structure, viz. this, $\overset{II}{Mn}<\begin{matrix}(Cl_2) \\ (Cl_2)\end{matrix}\!\!>\overset{IV}{MnCl_2}$, in which two double chlorine atoms act as a bivalent element or radical.

On the action of concentrated hydrochloric acid on manganese dioxide.—The action of strong hydrochloric acid on manganese dioxide has also been carefully studied by Franke, and in the light of the results obtained the old view of the formation of chlorine by this reaction is no longer tenable, and the changes which take place and which lead to its formation can best be represented by the following equations:

I. $O=\overset{IV}{Mn}=O+6HCl=\begin{matrix}H-(Cl_2)\\H-(Cl_2)\end{matrix}>\overset{IV}{Mn}=Cl_2+2H_2O$;

II. $\begin{matrix}H-(Cl_2)\\H-(Cl_2)\end{matrix}>\overset{IV}{Mn}=Cl_2=2Cl+MnCl_2+2HCl$;

III. $MnCl_2+\begin{matrix}H-(Cl_2)\\H-(Cl_2)\end{matrix}>\overset{IV}{Mn}.Cl_2=\overset{II}{Mn}<\begin{matrix}(Cl_2)\\(Cl_2)\end{matrix}>\overset{IV}{Mn}=Cl_2+2HCl$;

IV. $\overset{II}{Mn}<\begin{matrix}(Cl_2)\\(Cl_2)\end{matrix}>\overset{IV}{Mn}.Cl_2+4H_2O=\overset{II}{Mn}<\begin{matrix}O\\O\end{matrix}>\overset{IV}{Mn}<\begin{matrix}OH\\OH\end{matrix}+6HCl$;

V. $\overset{II}{Mn}<\begin{matrix}O\\O\end{matrix}>\overset{IV}{Mn}<\begin{matrix}OH\\OH\end{matrix}+8HCl=MnCl_2+\begin{matrix}H-(Cl_2)\\H-(Cl_2)\end{matrix}>\overset{IV}{Mn}=Cl_2+4H_2O$.

This reaction would go on repeating itself until at the end we should have left a strongly acid solution of manganous chloride, $MnCl_2$.

J. H. K.

The Union of Bodies by Pressure.

In former numbers of this Journal[1] attention has been called to the experiments of W. Spring and others upon the chemical reactions which take place between solid bodies under pressure. In the experiments described, Spring apparently succeeds in showing that solid bodies, finely pulverised and thoroughly mixed, unite chemically under pressure and produce a new compound, the amount of which is dependent upon the perfection and duration of contact of the original substances and the intimacy of their mixture.

The continuation of these experiments by the same investigator has yielded results which are of considerable interest. In his earlier work Spring[2] made use of simple substances; in his later work compound substances are used. Mixtures of dry pure precipitated barium sulphate and sodium carbonate were subjected to the influence of a pressure of six thousand atmospheres under various conditions of temperature and duration of contact. In each experiment about one gram of a mixture, composed of one part of barium sulphate and three parts of sodium carbonate, was used. The product obtained as a result of the pressure was

[1] **6**, 129 and 212. [2] Bull. Soc. chim. (Paris), 1885, **44**, 166.

thoroughly washed and the amount of barium carbonate in the insoluble residue was determined.

As in the case of the formation of sulphides and arsenides,[1] it was found that the percentage of barium carbonate produced by the action of sodium carbonate on barium sulphate under pressure, increases with the increase in the number of times the mixture is compressed. After a single compression the amount of barium carbonate produced was about one per cent. If the solid block produced by this compression is ground into fine bits and again subjected to the same pressure, and the process repeated a second time, about five per cent. of barium carbonate results. A sixth compression yielded nine per cent. of the product. These experiments show clearly the effect of a renewal of the faces of contact of two bodies capable of reacting under pressure. If the little blocks obtained by one, three and six compressions are left to themselves for some days and are then examined, it is found that, up to a certain limit, reached in about fourteen days, the amount of barium carbonate formed increases with the length of time during which the blocks have existed. The percentages found by Spring are:

Block produced at	0 days.	7 days.	14 days.	21 days.	28 days.
First compression,	.94	1.60	3.08	3.94	3.84
Third "	4.78	6.78	9.01	...	9.15
Sixth "	8.99	9.94	10.89	...	11.08

This result, Spring thinks, is difficult to explain, unless we attribute to matter the power of diffusion, even when in the solid state.

The effect of heat is next examined, and, contrary to expectation, it is found that those blocks which, when allowed to remain for fourteen days at ordinary temperatures, contained 9.01 and 10.89 per cent. respectively, after being heated three hours at 120° contain only 7.07 and 9.89 per cent. of barium carbonate. Hence we are justified in concluding that heat is not the direct cause of the reactions set up in these mixtures.[2]

Spring[3] next reverses the reactions. He mixes three parts of dry sodium sulphate with one part of barium carbonate, and subjects this mixture to a pressure of six thousand atmospheres as before. When subjected to a single compression, 59.16 per cent. of the barium carbonate passed over into the sulphate. Three compressions yielded 69.25 per cent. of the sulphate, and six give 73.31 per cent. As the mere shaking of a mixture of the two salts in the proportions used produced 49.79 per cent. of barium sulphate, the difference between this figure and those given above will represent the effect upon it of one, three and six successive compressions. The length of time during which the two substances are allowed to remain in contact exerts quite as marked

[1] Cf. this Journal **6**, 213. [2] Cf. this Journal **6**, 132. [3] Bull. Soc. chim. (Paris), 1886, **46**, 299.

an influence upon the amount of the new product formed as was noted in the former case. Here, too, there appears to be a limit beyond which the reaction refuses to proceed. The results obtained in this series are as follows:

Block produced at	0 days.	7 days.	14 days.
One compression,	59.16	63.91	64.66
Three compressions,	69.25	74.98	77.38
Six compressions,	73.31	80.68	80.31

When the little block produced by one compression is kept at a temperature of 160° for six hours, it is found to contain only 34.66 per cent. of barium sulphate instead of 59.16 per cent. The block produced by six compressions now contains only 46.38 per cent. instead of 73.31 per cent. These results substantiate those obtained in the first series, and show plainly that the reactions which have taken place cannot be due to a rise in temperature during the process of compression.

From a consideration of these two sets of experiments Spring regards as fairly well established the facts that—

1. Diffusion may take place as well in solid bodies as in those which are fluid.

2. Matter assumes under pressure a condition relative to the volume it is obliged to occupy.

3. For the solid state, as for the gaseous, there is a critical temperature, above or below which changes by simple pressure are no longer possible.

Liquid bodies, then, become solidified if their specific volumes are smaller in the solid than in the liquid state, and conversely, provided that in each case the critical temperature is taken into account. These results of Spring's are accepted by most chemists as worthy of very careful consideration. Mr. Hallock,[1] however, has recently criticised both the experiments and the conclusions of the French chemist, but as he seems to have misunderstood[2] Spring's position, and even his very language, a great deal of weight will not be attached to his criticism. W. S. B.

Germanium.

The scarcity of the material in which this element occurs has prevented a very active study of its properties and compounds; nevertheless, certain recent advances have been made along this line, and these are deserving of careful notice.[3] Winkler's latest experiments have had to do especially with the compounds of germanium with monatomic elements or radicals, such as the halogens, the alcohol

[1] Am. J. Sci. **34** (1887), 277. [2] Ibid, **35** (1885), 78, and Bull. Soc. chim. (Paris), **48**, 630.
[3] J. prakt. Chem. **36**, 177.

radicals, and hydrogen. As the author says,[1] "These experiments are still incomplete; nevertheless they may serve as the starting points for further investigation, and even in their present state throw a good deal of light on the chemical character of germanium."

Germanium dichloride, $GeCl_2$.—This compound has not as yet been obtained in pure condition. Attempts to make it by passing hydrochloric acid gas over heated germanium have resulted in the formation, not of the dichloride, but of germanium chloroform, $GeHCl_3$.

Germanium tetrachloride, $GeCl_4$.—This compound can best be prepared by gently heating a mixture of germanium sulphide and mercuric chloride. The resulting fluid remains liquid at a very low temperature and does not solidify at —100°.

Germanium chloroform, $GeHCl_3$.—This compound is prepared by passing dry hydrochloric acid gas over heated germanium. It is a colorless liquid which quickly becomes milky on exposure to air and also when distilled. This change is probably due to oxidation which results in the formation of an oxychloride, $GeOCl_2$.

Germanium oxychloride, $GeOCl_2$ (?).—This compound is probably formed by oxidation of germanium chloroform. As yet it has never been obtained in a condition sufficiently pure for analysis.

Germanium tetrabromide, $GeBr_4$.—When gently heated, germanium burns in bromine vapor with a pale yellow flame. The compound thus formed is the tetrabromide. It can be best prepared by heating together powdered germanium and mercuric bromide. In this way it is obtained as a clear, limpid, strongly fuming liquid which at 0° solidifies to a white crystalline mass.

Germanium difluoride, GeF_2.—This compound has not been isolated as yet, though there are some facts which speak for its existence.

Germanium tetrafluoride, GeF_4.—This compound is formed by treating germanium oxide with hydrofluoric acid. It crystallises from its thick, syrupy solution in white wart-like crystals which are very deliquescent. This conduct is similar to that of titanium fluoride, with this exception, that titanium fluoride and also zirconium fluoride give insoluble oxyfluorides when dissolved in cold water, whereas germanium fluoride forms a clear solution. Germanium fluoride is found to have the composition represented by the formula $GeF_4.3H_2O$. When heated with water it passes over partly into an oxyfluoride, and when the salt is heated to the boiling point of sulphuric acid it is partially decomposed into hydrofluoric acid and germanium oxide, but a portion of the compound passes off unchanged in the form of vapor.

Hydrofluogermanic acid, H_2GeF_6.—This compound is made by conducting the vapors of germanium fluoride, GeF_4, into water. In this way a clear liquid is obtained having a strong acid reaction. On allowing this liquid to evaporate spontaneously a thick acid

[1] J. prakt. Chem. **36**, 188.

liquid is obtained, from which small crystals of germanium oxide separate. Caustic potash and potassium salts cause a rich precipitation of the double fluoride of germanium and potassium from the acid liquid.

Potassium-germanium fluoride, K_2GeF_6.—This salt can easily be prepared by adding a concentrated solution of potassium chloride to a solution of germanium oxide in hydrofluoric acid. It is found to crystallise in the hexagonal system and, according to Krüss and Nilson,[1] it is isomorphous with the ammonium-silicium fluoride, $(NH_4)_2SiF_6$. Like the corresponding silicium compound it is found to be anhydrous, while the double fluorides of titanium, zirconium, and tin contain one molecule of water of crystallisation.

Compounds of germanium with alcohol radicals.—In his paper on the periodic law Mendelejeff,[2] predicting the properties of eka-silicium, says that "a slight difference between eka-silicium and titanium will consist in the fact that this element, like silicium and tin, will be able to form volatile metallo-organic compounds, whereas titanium can form no such compounds; and further, judging from the properties of silicium and tin, the ethyl compound of eka-silicium will boil at 160° and have a density of about 0.96." This prognostication has been verified in a remarkable way, and there can be no doubt that this hypothetical eka-silicium of Mendelejeff and germanium are the same element.

Germanium ethyl, $Ge(C_2H_5)_4$.—This compound is obtained by treating germanium tetrachloride with zinc ethyl. It is a colorless liquid of a weak leek-like odor; its specific gravity is slightly less than that of water, and it boils at 160°. At ordinary temperatures it is not acted on by the oxygen of the air; it is easily ignited, however, and burns with a dark yellowish-red flame. Its vapor forms explosive mixture, with oxygen.

Germanium ultramarine (?).—When germanium oxide is fused with soda and sulphur in a porcelain crucible, a small quantity of a blue compound is formed which is believed to be a germanium ultramarine. Attempts to prepare this in quantity have, however, resulted in failure. J. H. K.

NOTE.

The Determination of Morphine in Opium.

The Austrian Pharmaceutical Society recently offered the following as a prize question:

A comparative examination of the best known methods for the determination of the quantity of morphine in opium, and, if pos-

[1] Ber. **20**, 1699. [2] Ann. Chem. (Liebig) Suppl. **8**, 200.

sible, the perfecting of a new and very simple method sufficiently accurate to meet the practical need.

The satisfactory treatment of this subject secured the prize to A. Kremel, whose paper is given below in abstract. Five grams of the opium powder are macerated in a small flask, with 75 cc. of lime water, for 12 hours, with frequent shaking; this is then filtered through a plaited filter. (The ratio 1 part of opium to 15 parts officinal lime water has been arrived at by practice, and in this way there is obtained a nearly neutral or slightly acid filtrate. Should the liquid after the maceration react alkaline, then less lime water should be used.) To 60 cc. of the filtrate, corresponding to 4 grams of opium, which is brought into a weighed flask of such a size as to be nearly filled by the ether and ammonia, there is added 15 cc. of ether and 4 cc. of normal ammonia. The flask is then well corked and the contents mixed by gentle agitation. The flask is then set aside for 6 to 8 hours, the temperature being kept at 10°–15°. At the end of that time the ethereal layer is removed, 5 cc. of fresh ether added, and the flask gently shaken; the ether is again removed, and finally the crystals of morphine, which have separated out, are collected on a small plaited filter. The crystals which remain in the flask are washed with 5 cc. of distilled water; this wash-water is brought on the filter, and finally the flask and also the filter and its contents are dried at 100°. The crystals on the filter are transferred to the flask, and this is then dried until a constant weight is obtained. The morphine thus obtained is perfectly pure, and dissolves *completely*, though slowly, in 100 parts of saturated lime water.

The mode of procedure is the same for opium extract, 1 part of extract is treated with 20 parts of lime water. Opium tincture is first mixed with powdered glass which has been washed with hydrochloric acid, and the mixture evaporated to dryness on the water-bath; the residue is then treated with a quantity of lime water equal to the quantity of tincture used in the experiment.—(*Pharm. Post.* 1887, **20,** 661; *Abstract in Chemisch. Repert. of the Chemiker Zeitung*, 1887, 258.)